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Bioavailability of Atmospheric Dissolved Organic Nitrogen in The Marine Aerosol over the Gulf of Aqaba

[1]M.A. Wedyan, [1]K.G. Fandi and [2]S. Al-Rousan

[1]Biological Department, Al Hussein Bin Talal University, Ma'an, P.O. Box 20, Jordan
[2]University of Jordan & Yarmouk University Marine Science Station,
P. O. Box 195, 77110 Aqaba, Jordan

Abstract: Atmospheric dissolved organic nitrogen (DON) has recently gained attention as a significant additional source of new N loading to the sea. Utilization of DON aerosol source by costal phytoplankton was examined in short-time scale (0-12 day) in the Gulf of Aqaba. The proportion of DON utilized ranged from 29-43%. Although phytoplankton production generally increased with aerosol DON addition, the increased production was not correlated (r^2=0.79) with amount of DON utilized suggesting that a variable portion of dissolved organic matter was directly or indirectly available to the phytoplankton. The effect of atmospheric N on marine productivity depends on the biological availability not on the amount of deposition of both inorganic and organic N. Event base measurements for coastal Gulf of Aqaba showed that about 80% of atmospheric deposition N was organic N. These results indicate that atmospheric DON in aerosol could be an important source N to the Gulf of Aqaba.

Key words: Dissolved organic nitrogen (DON), aerosol, phytoplankton and Gulf of Aqaba

INTRODUCTION

Atmospheric deposition can be an important source of nutrients to marine ecosystems and much recent attention has focused on the deposition of organic nitrogen (Cornell *et al.* 2001; Neff *et al.* 2002; Zhang and Anastasio 2003). Recently, the inorganic nitrogen species (i.e., NO_3^- and NH_4^+) considered to be an important in the transport and deposition of nitrogen in the atmosphere and have been extended to organic nitrogen compounds (Cornell *et al.* 1995; Seitzinger and Sanders 1999; Wedyan 2005). Because nitrogen is the primary nutrient-limiting plant, algal and microbial production in many terrestrial and marine environments, as well as some freshwater environments, increases nitrogen inputs can markedly alter those ecosystem (Vitousek and Howarth 1991). Atmosphere may be particularly important in oligotrophic ocean (Owens *et al.* 1992). Specifically, the dry deposition of atmospheric nutrients to the Gulf of Aqaba may support a large fraction of new production in the photic zone due to negligible river runoff and precipitation (Ganor and Fones 1996). The pervious studies suggested that organic nitrogen compounds influence atmospheric chemistry and contribute to the nutrient budgets of land and marine ecosystems. Deposition of organic nitrogen in seawater from atmosphere can increase the productivity of the primary producer, since a major fraction of the dissolved organic nitrogen (DON) supplied by rainwater is found to be biologically available (Ogawa and Tanoue 2003). The DON increases total N deposition from ~30 to ~40% for coastal areas worldwide (Duce, 1998). In addition, the air borne organic nitrogen (i.e., amino acids and urea) investigations are very important from the cloud chemistry point of view as it is associated with particulate organic carbon (Saxena and Hildemann 1996; Saxena *et al.* 1995).

Currently, not much information on the composition and source of organic N in aerosols is available to understand the transport and bioavailibility of atmospheric nitrogen species and their effect in the Gulf of Aqaba ecosystem. This is true for DON over the remote marine atmosphere, since organic N contributes significantly in remote atmosphere, about ~ 31 and ~ 64 % of the total N under clean marine and dirty continentally affected conditions, respectively (Cornell *et al.* 2001). DON from rainwater collected in coastal north Carolina was shown to stimulate phytoplankton production and, in some cases, biomass over short-time scales (24- 48h) (Peierls and Paerl 1997).

The aim of the present study is to examine how much of the DON in marine aerosol collected over the Gulf of Aqaba is potentially available for use by marine phytoplankton and the potential effect of aerosol DON on phytoplankton production.

Corresponding Author: Moh'd Wedyan, Biological Department, Al Hussein Bin Talal University, Ma'an, P.O. Box 20, Jordan
E-Mail: mwedyan@ahu.edu.jo

MATERIALS AND METHODS

Study Area:

The Gulf of Aqaba is located in the southern of Jordan (Fig. 1). The sampling site (approx. 3-5 m from ground level and approximately 40 m from the road side) is close to the city centre, with an open aspect in all directions.

Fig. 1: Aerosol sampling location (29° 50¢N, 35° 00¢E) at south of Jordan.

Sampling Collection and Analyses:

Aerosols were collected by aerosol trap. The collected aerosols were stored in plastic bags. The aerosols dissolved in deionized water (specific resistivity > 18 MΩ cm) and filtered through a per-combusted glass fiber filter (whatman GF/F). Subsamples from the filtrate were frozen separately from each sample for subsequent analysis of dissolved inorganic nitrogen (DIN) species (NO_2^-, NO_3^- and NH_4^+) and total dissolved nitrogen (TDN) analyses *(see below for method).* Procedural blanks of distilled-deionized water were analyzed for DIN species and TDN to check for possible contamination from the collection and storage procedures. No measurable contamination was detected.

Bioavailability Experiments:

The biological availability of DON in the aerosol and its effects on coastal phytoplankton productions were examined by added aerosol DON to seawater and following the response of the phytoplankton production and the changes in DON and DIN concentrations.

Time-series samples of the microcosm water were collected on day 0,3,6,9 and 12 and analyzed for NH_4^+, $NO_2^- + NO_3^-$ using the method described by (Parsons *et al.* 1984) and total dissolved nitrogen (TDN) was also measured (Walsh 1989). DON was determined by the difference between TDN and dissolved inorganic nitrogen (DIN= $NH_4^+ + NO_2^- + NO_3^-$). Phytoplankton production [Chlorophyll-a (chl-a) concentration] was measured using the spectrophotometer (Strickland and Parsons 1972).

RESULT AND DISCUSSIONS

The proportion of DON utilized by the phytoplankton likely depends on a number of factors, including differences in the chemical composition of the source material and the organisms present to utilize the DON, as well as physical condition and exposure time. The bioavailable term DON was used in this study to refer to the DON that was utilized by the phytoplankton over 12 day time period under our experimental condition. In the current study, phytoplankton production in the coastal water increased linearly with addition of DON (r^2= 0.77) (Fig. 2). There was a consistent quantitative relationship between increased phytoplankton production and the amount of DON utilized in the treatment. This suggests that a variable portion of the DON was directly or indirectly (through microbial mineraliztion) reaching the phytoplankton. The duration of the experiments (approximately 2 weeks) was long compare to the generation time of bacteria or bacterial grazers and thus should have been sufficient for microbial mineraliztion of DON utilized by the bacteria. The results of the current study also provide insight into the interpretation of data from other approaches that have been used to measure DON bioavailability (Seitzinger *et al.* 2002).

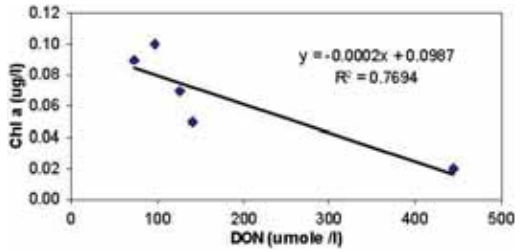

Fig. 2: Relationship between phytoplankton production (Chl. a) and DON utilization in the bioavailability experiment.

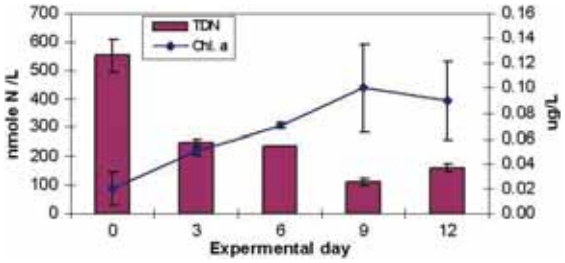

Fig. 3: Biomass results showing the response of Phytoplankton (Chl. a) to TDN.

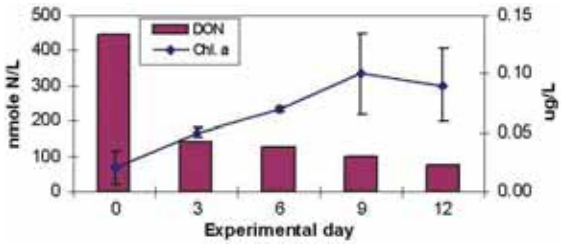

Fig. 4: Biomass results showing the response of phytoplankton (Chl. a) to DON.

Table 1: Comparison of the aerosol DON from different locations.

Location	% DON	Reference
UK	21	Cornell, *et al*. (1995)
Bermuda	59	Cornell, *et al*. (1995)
Tahiti	84	Cornell, *et al*. (1995)
NE Atlantic	67	Cornell, *et al*. (1995)
Philadelphia, PA	19-52	Seitzinger and Sanders (1999)
The Gulf of Aqaba	46-80	This study

The proportion of DON was 46 - 80% which is biologically available. Comparing this finding (aerosol over the Gulf of Aqaba) with the data from wide range locations demonstrate that DON is an important fraction in the atmospheric TDN (Table 1).

Figure (3) was shown the phytoplankton response to the TDN concentration in the aerosol sample. This study represents that ~20- 45% of TDN was utilized by phytoplankton in 12 days period. There was rapid disappearance of aerosol TDN with increase in growth and production of phytoplankton. The increasing difference between the cumulative amount of TDN added and the amount of TDN remaining in the bioavailable experiments during the 12 days of additions indicates rapid utilization of aerosol TDN.

The phytoplankton response to the aerosol DON has shown the same pattern of the response to the TDN (Fig. 4). By day 3, 29% of the DON had been utilized while by day 12, 43% had been utilized. However, it appears that there was no further net uptake of DON, because by the next measurement (day 15), the difference between the concentration of DON added and DON remaining was essentially the same as on day 12. Phytoplankton production and particularly phytoplankton biomass (chl. a) were greater in the DON addition relatively to controls which is constant with the other studies (Seitzinger and Sanders 1999; Seitzinger *et al.* 2002). These results suggesting that DON initially in the costal water was recalcitrant and / or was replaced by internal DON production.

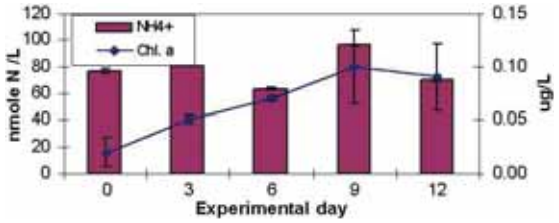

Fig. 5: Biomass results showing the response of phytoplankton (Chl. a) to NH_4^+.

The addition of atmospheric DIN, particularly NH_4^+ addition, increased phytoplankton production (Fig. 5). Stimulation phytoplankton biomass (chl. a) is consistent with the high percentage of DON disappearance (~67%), which is attributed to phytoplankton utilization. These responses are in the range of reported in the literature(Antia *et al.* 1991; Seitzinger *et al.* 2002).

As the previous analyses have suggested that the atmosphere is an important source of N to a range of marine ecosystems (Nakamura 2006; Nakamura *et al.* 2005; Paerl and Whitall 1999; Wedyan 2005). However, most studies have considered only atmospheric DIN inputs. Those studies that included both DIN and DON (Cornell *et al.* 2003; Scudlark *et al.* 1998) did not asses how much of DON was biologically available. On the other hand, our results show that the atmospheric DON can be used to enhance short- term phytoplankton growth. The consequence of this extra combined N on longer term (i.e. weeks to months) and larger scale marine biogeochemical processes requires further clarification. Also, the current study suggests that development of biologically available N budgets for ecosystems requires measurements of both inorganic N deposition and that component of organic N deposition that is bioavailable, this is consistent with the growing number of studies that demonstrate the dynamic role of dissolved organic matter in aquatic ecosystems (Seitzinger *et al.* 2002).

Conclusion:

Increased N inputs to terrestrial and aquatic ecosystems results in a variety of environmental problems (Seitzinger and Sanders 1999; Valiela *et al.* 2000). The present study suggests that one of the sources of DON was belonged to be anthropogenic source (particularly human activities) that contribute ~ 80% of the TDN over the Gulf of Aqaba. This is a significant fractions of the DON in atmospheric deposition is biologically available and furthermore that this bioavailable DON can be an important component of N inputs compared to other sources to marine ecosystems. Furthermore, the importance of atmospheric DON depends not only on the deposition quantity, but also on the availability of the N as a nutrient for phytoplankton. In order to have an adequate understanding of the cycling of atmospheric nitrogen information about other component of the cycle is needed.

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