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Significance of Dissolved Nucleic Acids in Dissolved Organic Phosphorus (DOP) Pool and Their Dynamics in Oceanic Phosphorus Cycle

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용존 유기인 중 용존 핵산의 중요성 및 대양 인 순환에서의 의미

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An analysis of collected data on components of dissolved organic phosphorus (DOP) and DOP is made to search for important components of DOP pool and their implications in phosphorus (P) cycling. The significance of dissolved nucleic acids (D-NA) apparently tends to increase with increasing trophic status of oceanic waters. Interestingly, the sum of all 5'-nucleotides and D-NA seems to dominate the DOP pool. Thus, mineralization of D-NA could be a significant pathway of P cycling in surface oceanic waters and it might be of great importance in lakes where P limits primary production. Processes related to death of microbes are responsible for D-NA and DOP production in surface waters, and incomplete digestion of preys by grazers seems to be an important mechanism in D-NA production.

용존 유기인 풀(pool)의 구성 성분과 그것들이 인 순환에 미치는 영향을 조사하기 위해 용존 유기인의 구성 성분과 용존 유기인에 대해 수집된 자료를 분석하였다. 용존 핵산은 대양수의 영양단계가 높아짐에 따라 그 중요성이 증가하는 것으로 보였다. 흥미로운 것은 전체 5'-뉴클레오티드와 용존 핵산의 합이 용존 유기인 풀을 우점하는 것으로 보인다는 것이다. 따라서 용존 핵산의 광물화는 대양 표층수에서 인 순환의 중요한 경로가 될 수 있으며 인이 일차 생산을 제한하는 호수에서 대단히 중요할 것이다. 용존 핵산과 용존 유기인이 생성되는 기작으로서 미생물의 사망에 관련된 프로세스들이 중요하며, 특히 용존 핵산의 생성에 있어선 포식자에 의한 먹이의 불완전 소화가 중요한 기작으로 사료된다.

INTRODUCTION

An understanding of compositions and dynamics of dissolved organic matter in aquatic ecosystems has been one of the major research in aquatic sciences (Watt and Hayes, 1963; Kuenzler, 1970; Minear, 1972; Lean, 1973; Butler *et al.*, 1979; Lemasson and Pages, 1981; Williams, 1986; DeFlaun *et al.*, 1987). During the last two decades, data on dissolved organic phosphorus (DOP, Holm-Hansen *et al.*, 1966; Banoub and Williams, 1972; Smith *et al.*, 1986), dissolved nucleotides (McGrath and Sullivan, 1981; Ammerman and Azam, 1985), dissolved nucleic acids (D-NA, DeFlaun *et al.*, 1987; Paul *et al.*, 1987; Karl and Bailiff, 1989), and dissolved phospholipids (Parrish and Wangersky, 1988) have been accumulated from diverse areas of the ocean. Thus, it becomes possible to address: 1) What are the major components of

Table 1. Literature values of dissolved organic phosphorus, DNA, RNA, ATP, phospholipids, and nucleotides in the sea

Compounds	Concentration	Regions	References
DOP (μg P l^{-1})	4.0-6.2	Hawaii	Smith *et al.* (1986)
	6.2-9.3	Central North Pacific gyre	Williams *et al.* (1980)
	6.2-12.4	Southern California Bight	Holm-Hansen *et al.* (1966); Jackson and Williams (1985); Ammerman and Azam (1985)
D-DNA (μg l^{-1})	1.0	Central Pacific gyre	Karl and Bailiff (1989)
	4.7	Kahana Bay	Karl and Bailiff (1989)
	10-19	Florida coastal water	DeFlaun *et al.* (1987)
D-RNA (μg l^{-1})	8.0	Central Pacific gyre	Karl and Bailiff (1989)
	20.6-31.9	Kaneohe Bay	Karl and Bailiff (1989)
	51.1	Kahana Bay	
D-ATP (μg l^{-1})	0.02-0.57	Oligo-to-eutrophic ocean	Hodson *et al.* (1981a, b) Azam and Hodson (1977)
D-Phospholipids (μg l^{-1})	1.1-15	Scotian shelf	Parrish and Wangersky (1988)
D-Nucleotides (μ moles l^{-1})	0.01-0.02	California coastal waters	McGrath and Sullivan (1981); Ammerman and Azam (1985)

DOP throughout oligotrophic to eutrophic oceanic waters?, 2) How can it be explained that DOP seems to be geochemically non-refractory?, and 3) By what mechanism are the major components of DOP produced?

DATA BASE AND DISCUSSION

1. DOP

All the data cited in this study of DOP and its components do not come from the same samples. Thus, comparison of any components of DOP with DOP can only be meaningful if DOP concentration is known to be relatively invariant in oceanic waters. In fact, DOP concentration in the oceanic waters seems to be uniform (Banoub and Williams, 1972; Smith *et al.*, 1986). The DOP concentration near Hawaii ranged from 0.13-0.2 μg-at P l^{-1} (Smith *et al.*, 1986). In central North Pacific gyre, DOP concentration ranged ca. 0.2-0.3 μg-at P l^{-1} (Williams *et al.*, 1980). Even in the meso-to-eutrophic Southern California Bight, where studies on dissolved organic matter have been done for a long time, DOP concentration ranges ca. 0.2-0.4 μg-at P l^{-1} in surface waters (Holm-Hansen *et al.*, 1966; Jackson and Williams, 1985; Ammerman and Azam, 1985, Table 1). Another interesting point about DOP in oceanic waters is its non-refractory characteristic (Jackson and Williams, 1985).

However, DOP data should be read carefully because GF/C filter traditionally used in the measurements of DOP will pass >95% of bacteria (Lee and Fuhrman, 1987; Cho, 1988). In typical seawater samples bacterial abundance would be 1×10^9 l^{-1}. If we use C:P ratio of 38.5 by atom (Gächter *et al.*, 1988) and 20 fg C $cell^{-1}$ (Lee and Fuhrman, 1987) in natural bacteria, then bacteria contribute 1.3 μg P l^{-1}, which can

Table 2. Calculations of turnover time of dissolved nucleic acids (D-NA) and dissolved organic phosphorus (DOP) in oligotrophic and eutrophic oceanic surface waters. Typical data of bacterial abundance, phytoplankton carbon, growth of bacteria and phytoplankton, D-NA and DOP concentrations were used. DNA content in phytoplankton was calculated by a factor of 0.5-1.5 μg DNA per 100 μg C in Phytoplankton (Holm-Hansen *et al.*, 1968). RNA:DNA ratio of 5.7in algäe (Mann and Carr, 1974) was used. DNA content in bacteria was assumed to be 3 fg per cell(Cho and Azam, 1988a) and same amount of RNA (Azam, personal communication) in bacteria. Ratio of 0.068 in P:C was used for bacteria (Gächter *et al.*, 1988) and 0.024 for phytoplankton (Redfield, 1963).

	Oligotrophic oceanic waters	Eutrophic oceanic waters
Bacterial carbon[1] (C)	10 μg C l^{-1}	20 μg C l^{-1}
Phytoplankton C[2]	5 μg C l^{-1}	100 μg C l^{-1}
Bacterial phosphorus (P)	0.68 μg P l^{-1}	1.4 μg P l^{-1}
Phytoplankton P	0.12 μg P l^{-1}	2.4 μg P l^{-1}
Bacterial nucleic acids	3 μg l^{-1}	6 μg l^{-1}
Phytoplankton nucleic acids	0.2-0.6 μg l^{-1}	3.9-11.6 μg l^{-1}
Generation time		
in bacteria[1]	10 days	1-2 days
in phytoplankton[3]	1 day	1 day
DOP concentration[4]	0.13-0.3 μg-at P l^{-1}	0.17-0.4 μg-at P l^{-1}
D-NA concentration[5]	9 μg l^{-1}	30 μg l^{-1}
Calculated		
D-NA turnover time	10-20 days	1.3-4.3 days
DOP turnover time	22-49 days	1.4-4.0 days

1. Cho and Azam (1988); Fuhrman *et al.* (1980), 2. Cho and Azam (1990); Eppley *et al.* (1977, 1988), 3. Laws *et al.* (1987), 4 & 5. in text.

be ca. 20% of DOP with 0.2 μg-at P l^{-1}.

2. *Components of DOP*

Dissolved nucleic acids: Dissolved DNA (D-DNA) concentration in the oligotrophic waters in the central Pacific gyre was ca. 1 μg l^{-1} and that of dissolved RNA (D-RNA) ca. 8 μg l^{-1} (Karl and Biliff, 1989). Since phosphorus content in D-DNA and D-RNA is 9.4% by weight, D-DNA and D-RNA would comprise 9-22% of DOP in oligotrophic waters with DOP of 0.13-0.3 μg-at P l^{-1}. The estimate of 9-22% would be conservative because possible adsorption of D-NA to glass-fibre filter was found to be important in oligotrophic samples (Paul *et al.*, 1987). In meso-to-eutrophic oceanic waters, there are limited measurements of D-RNA. However, based on a few values of D-NA data from Kaneohe Bay (Karl and Bailiff, 1989), P content in D-NA would comprise 17-53% of P content in DOP (typical coastal DOP concentration of 0.2-0.4 μg-at l^{-1} was used). This estimated contribution of D-NA to P pool in DOP might be conservative because GF/C filter was used in most past studies of DOP. This calculation indicates an increasing importance of D-NA as P source in DOP with increasing trophic status, and suggests that DNA is the greatest pool among the known DOP components in the ocean (Table 1). The fact that apparently increasing significance of D-NA in DOP with increasing trophic status is consistent with the increasing biomass of microbes with increasing trophy of oceanic waters (Table 2). Thus, processes related to death of microbes are implicated to DOP and D-NA production and cycling of P in the ocean (see below).

The concentration of dissolved ATP (D-ATP) in oceanic waters from oligotrophic to eutrophic waters ranges 22-568 ng l^{-1} (Hodson *et*

al., 1981a; Azam and Hodson, 1977) and represents a small pool of DOP since P content in ATP is 18.5% by weight. However, if we add all the 5'-nucleotides (ca. 10-20 n moles l^{-1}, Ammerman and Azam, 1985; McGrath and Sullivan, 1981), the concentration of all the 5'-nucleotides is a significant source of P in DOP pool. Thus, dissolved nucleotides and nucleic acids can be dominating pools of DOP, and D-NA can be substantial sources of substrates for activity of the 5'-nucleotidase (Ammerman and Azam, 1985) in natural bacteria.

Dissolved phospholipids: A limited studies of the distribution of phospholipids in pelagic ocean (Parrish and Wangersky, 1988) indicate that these chemicals can vary on the order of magnitude from 1.1-15 μg l^{-1}. If we assume average molecular weight of 700 and one atom of P present per phospholipid, then 0.05-0.7 μg P l^{-1} is in dissolved phospholipid which is ca. 1% of DOP.

Thus, it seems that D-NA, dissolved nucleotides, and phospholipids can explain the pool size of the previously measured DOP in sea water. Since these compounds are all biologically active, this will explain why DOP is not refractory (Jackson and Williams, 1985).

3. DOP production

Direct measurements of dissolved DNA (D-DNA) turnover (Paul *et al.*, 1987) indicate a fast turnover of D-DNA in eutrophic waters (< 1 day) and a slow turnover in oligotrophic waters (*ca.* 32 days). This indicates presence of mechanisms by which D-DNA and D-NA are supplied. Since most of particulate DNA is in bacteria in the ocean (Paul and Carlson, 1984), the major supply of D-DNA must come from bacteria, presumably via processes related to death of bacteria (Paul *et al.*, 1987). Also, it can be envisaged that processes related to death of bacteria and phytoplankton are mechanisms of D-RNA production. Calculations of turnover time of D-NA and DOP are made for oligotrophic and eutrophic oceanic surface waters by using typical data of bacterial abundance, phytoplankton carbon, growth of bacteria and phytoplankton, and D-NA and DOP concentrations (Table 2). The calculation is based on a simple assumption that all microbial nucleic acids and organic phosphorus produced become to be dissolved. In other words, no inorganic phosphate is produced. This assumption does not sound perfect, but the results show that the calculated DOP turnover time and D-NA turnover time are surprisingly similar to the reported ones in oligotrophic and eutrophic oceans (Paul *et al.*, 1987; Jackson and Williams, 1985). The consistency found between the calculated and the reported DOP and D-NA turnover times indicates that processes related to death of preys by grazers produce D-NA and DOP. Further, the above results suggest that in oligotrophic ocean, where sloppy feeding by macrozooplankton would be minimal, solubilization of particulate P (in microbes) via incomplete digestion of preys by micrograzers seems to be important mechanism of DOP and D-NA production. This suggestion is also consistent with the molecular structures of DNA and RNA in cells. DNA is postulated to be very compactly packaged in natural bacteria (Cho, unpublished manuscript). Further, DNA and RNA are associated with histone-like proteins and ribosomal proteins, respectively. Thus, within limited digestion time during grazing in animals, DNA and RNA might be partially digested because of steric hinderance of the associated proteins. Thus, it would be possible to release some DNA and RNA by grazers after digestion of the prey-microbes. This conclusion is similar to a recent idea on dissolved organic carbon pathway in the sea by Jumars *et al.* (1989), who regards incomplete ingestion, digestion, and absorption as the major mechanism for production of dissolved organic carbon for bacterial growth.

4. DOP in the P cycling

Since D-NA is a P and N rich molecule and comprises a large fraction of DOP in eutrophic aquatic systems, D-NA as P and N sources would be significant in lake systems in which P is normally limiting primary production. The study on regulation of conversion of DOP as well as D-NA to inorganic phosphate should be carried out because DOP concentration at least does not change noticeably during annual cycle. Many mechanisms are known to be responsible for producing dissolved organic matter in the sea (Azam and Cho, 1987). However, in natural waters, no mechanisms in organic matter production has yet been quantified. This indicates the difficulty associated with the measurements. More studies have to be done in future to understand which mechanism is the most important one in dissolved organic matter production.

CONCLUSION

Dissolved nucleic acids seem to have increasing their significance as constituents of DOP with increasing trophic status of oceanic waters. Production of D-NA would be due partly to incomplete digestion of prey-microbes by grazers. Further, phytoplankton seems to be a major source of D-RNA in eutrophic waters. In future, studies on regulation of turnover of dissolved nucleotides and D-NA will be interesting subjects, especially in freshwater ecosystems, biochemistry of microbial growth, and biogeochemical cycles of P and N.

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