Nitrogen and Phosphorus in Coastal Systems: Focus on Dissolved Organic N and P

Daisy O. Padayao* and **Maria Lourdes San Diego-McGlone**
Marine Science Institute, College of Science
University of the Philippines, Diliman, Quezon City 1101 Philippines
Tel. No.: (632) 922-3944; Fax: (632) 924-7678; E-mail: daisyp@upmsi.ph

ABSTRACT

Quantification of dissolved organic phosphorus (DOP) and dissolved organic nitrogen (DON) levels, and the relative importance of the organic fraction at various habitats (river, seagrass bed, mangrove area, coral reef, fishpen, and ocean) were the focus of this study. DON concentrations ranged from 9.5 to 44.3 µM during the dry season and from 10.9 to 23.7 µM during the wet season. DOP values ranged from 0.3 to 0.4 µM during the dry season and from 1.0 to 1.6 µM during the wet season. DON was 70-90% of the dissolved fraction in the first five habitats for both dry and wet seasons. DOP was approximately 15-35% during the dry season and 50-60% during the wet season. DON was highest in the river and lowest in the coral reef area for both seasons. High DOP concentrations were determined in the river and mangrove area in the dry season while lowest values were seen in the coral reef area. During the wet season, DOP was highest in the coral reef area and lowest in the mangrove area. When compared with oceanic systems, dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorus (DIP) have higher percentages (25-58% for DIN and 71-83% for DIP) in the open ocean than in coastal areas (10-32% for DIN and 62-67% for DIP). However, DON and DOP were the dominant forms in the coastal sites (42-75% DON vs 7-32% DIN and 17-30% DOP vs 35-67% DIP). The smaller fraction of the organic forms of N and P in the open ocean may be indicative of the greater efficiency in nutrient recycling/regeneration in the open ocean than in the coastal area. N:P ratios in the five habitats ranged from 2 to14 with the highest ratio in the coral reef area.

Keywords: dissolved organic nitrogen (DON), dissolved organic phosphorus (DOP), dissolved inorganic nitrogen (DIN), dissolved inorganic phosphorus (DIP), coastal habitats

INTRODUCTION

Nutrient studies conducted in coastal systems often determine only the inorganic fraction of nitrogen (NH_3, NO_3, NO_2) and phosphorus (PO_4). Little attention has been given to the organic fraction, which, from previous works constitutes a large portion of the total dissolved N and P in the water column (Jacinto 1992).

A comprehensive understanding of the nutrient cycle requires knowledge of the various forms and transformations undergone by nitrogen and phosphorus. The roles of the organic fractions of N and P in the nitrogen and phosphorus cycles have been well illustrated (Parsons and others 1984b). The major constituents of total dissolved nitrogen (TDN) are the dissolved inorganic nitrogen (DIN) and the dissolved organic nitrogen (DON). DON can come from external inputs via runoffs or through the fixing of DIN. Inorganic nitrogen sources include precipitation and the fixing of N_2 gas from the atmosphere. This inorganic N

* *Corresponding author*

is transformed to particulate organic nitrogen when taken in by organisms, and through bacterial action during decomposition, it is converted into DON. DON can then be used directly by organisms as food source in the form of urea and amino acids, or it can be converted into the inorganic form via bacterial action (Parsons and others 1984b).

Total dissolved phosphorus (TDP) is partitioned between dissolved inorganic phosphorus (DIP) and dissolved organic phosphorus (DOP) (Orrett and Karl 1987). It is apparent from the phosphorus cycle that the various forms of phosphorus are often readily exchangeable as metabolites. Soluble inorganic phosphorus is taken up by organisms that release dissolved organic phosphorus as an excretion product. Similar to DON, DOP can be directly assimilated by organisms or it can be converted back into its inorganic form through bacterial action (Parsons and others 1984b).

DON and DOP are poorly characterized compounds but are present at elevated concentrations (Jackson and Williams 1985). Hence, it is important to quantify their potential contributions to the nutrient pool and better understand their roles in the N and P cycles. This study was undertaken to quantify levels of DON and DOP from various habitats (i.e., seagrass bed, fishpen, coral reef, mangrove, river, ocean) in order to assess their importance in different systems, and relate these fractions to the inorganic forms of N and P.

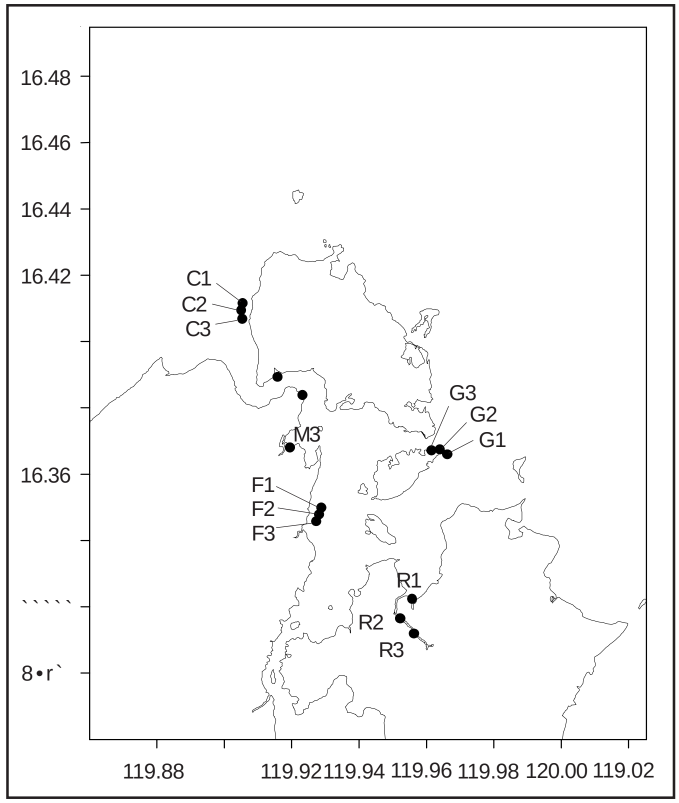

Fig. 1. Map of stations in Bolinao, Pangasinan during the dry and wet seasons; sampling. (R1, R2, R3 = river stations; S1, S2, S3 = seagrass stations; F1, F2, F3 = fishpen stations; C1, C2, C3 = coral stations; M1, M2, M3 = mangrove stations)

MATERIALS AND METHODS

Water samples were collected during the dry (May 3-6, 1999) and wet (August 25-26, 1999) seasons from 5 different habitats in Bolinao, Pangasinan: (1) river, (2) seagrass bed, (3) fishpen, (4) coral reef, and (5) mangrove area. Three sites were sampled from each of the habitat (Fig. 1). Samples were taken at 1 m depth using a 5 L Niskin sampler.

Samples for DIN, DON, DIP and DOP determinations were filtered through Whatman GFC filters, stored in high density polyethylene (HDPE) bottles and kept frozen until analysis in the laboratory. Inorganic N and P were determined using methods described by Parsons, et al. (1984a). TDN and TDP were analyzed after persulfate oxidation using the methods of Koroleff (1983). DON and DOP were operationally defined as the difference between TDN and DIN, and TDP and DIP, respectively.

RESULTS AND DISCUSSION

Nitrogen constituents

Fig. 2 shows the horizontal distribution of nitrogen constituents during the dry and wet seasons. The highest DIN concentrations which were measured in the river in both seasons could be due to external inputs, such as waste discharges. The high concentrations of DIN in the mangrove area could be due to the inputs of a small river system in this area. High concentrations of DON

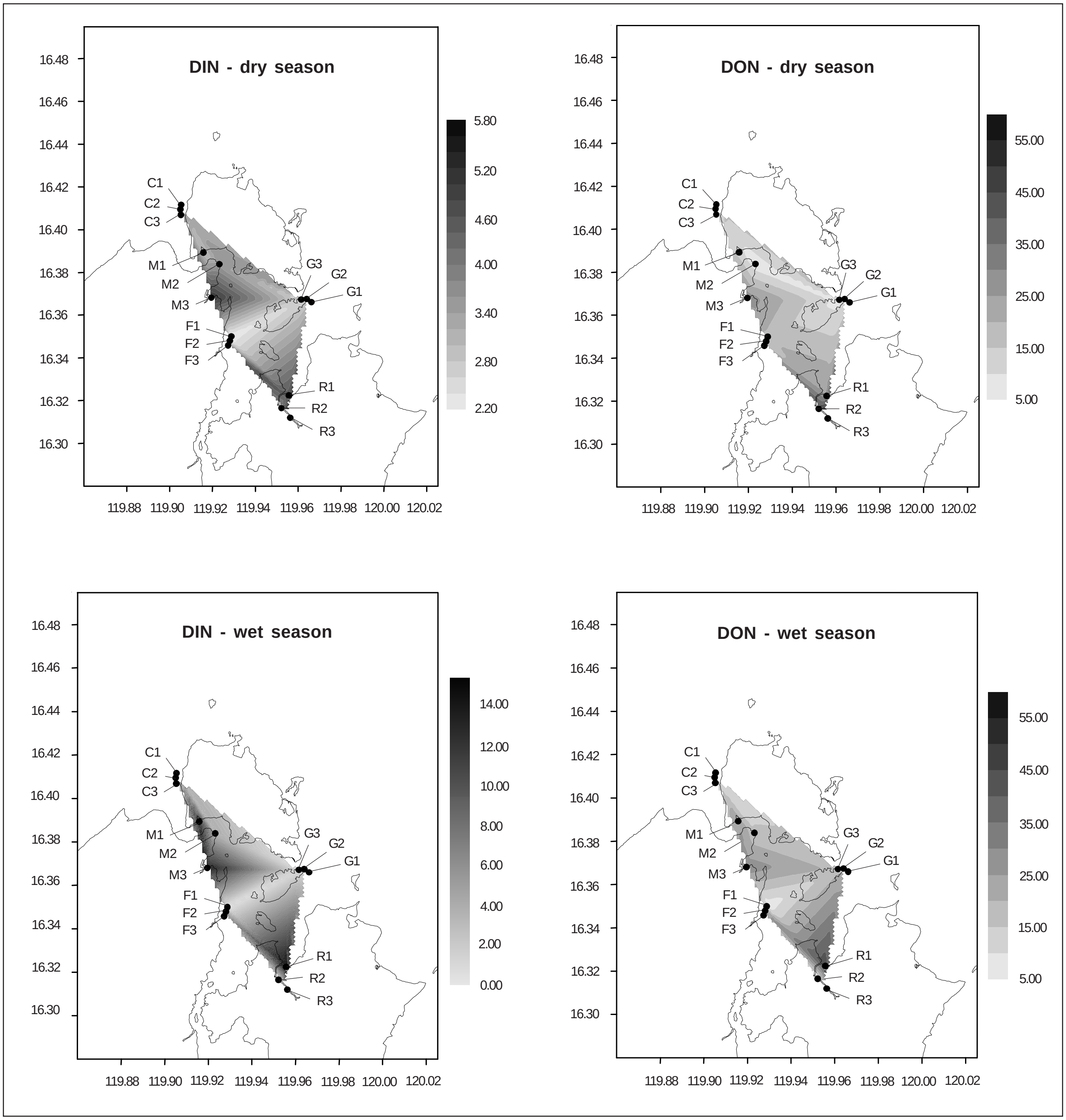

Fig. 2. Horizontal distribution of the nitrogen constituents during the dry and wet seasons

were, likewise, observed in the river area during both seasons, albeit concentration gradients for DON were less defined than DIN. Levels of DIN and DON in all habitats in both seasons are shown in Fig. 3. DIN and DON were consistently higher in the river area. DIN concentrations were lowest in the seagrass beds, while DON was lowest in the coral reef area. DIN and DON concentrations were higher during the wet season.

Table 1 summarizes the average concentrations of the N constituents from the five habitats. The ranges of DIN concentration were 3.05 to 4.44 μM and 1.23 to

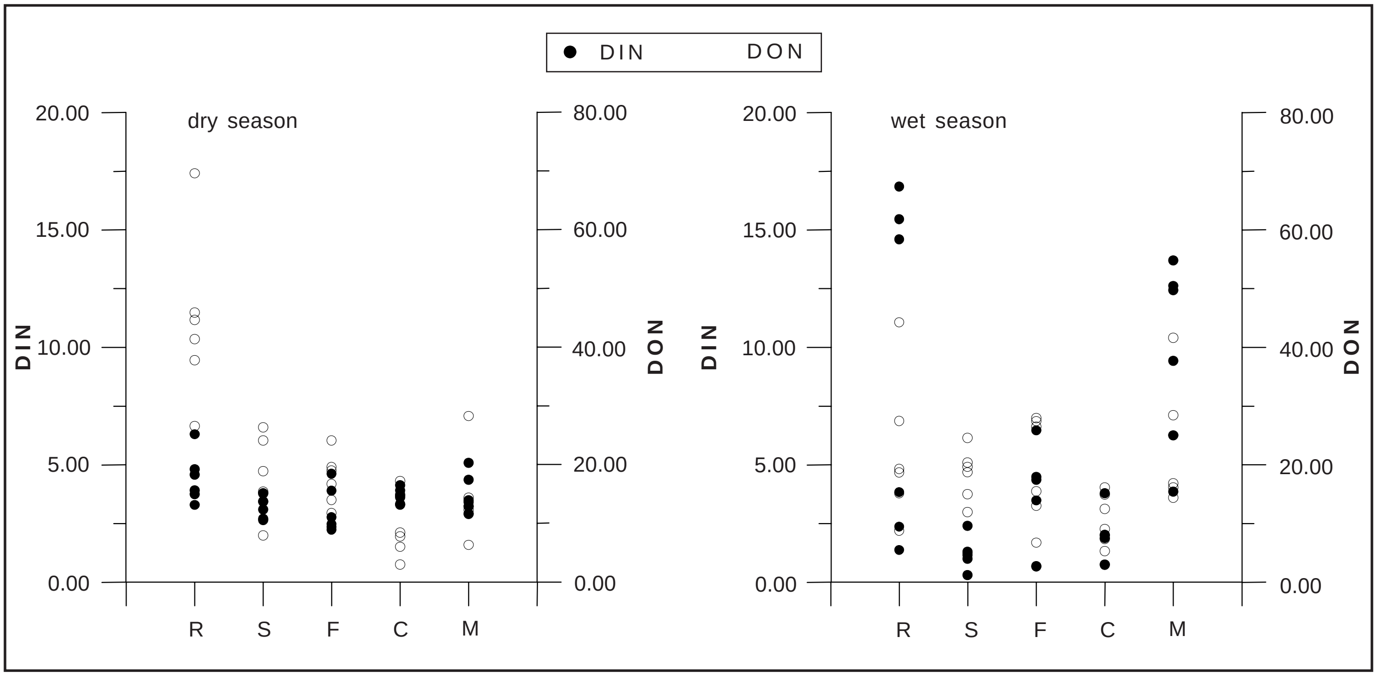

Fig. 3. Concentration of DIN and DON in the five habitats (R-river; S-seagrass; F-fishpen; C-coral reef; M-mangrove) during the dry and wet season

Table 1. Mean concentrations of the N constituents in the five habitats during the dry (May) and wet (August) seasons. (Values expressed in µM) *DIN is $NO_3 + NO_2 + NH_3$

	Dry			Wet		
Sampling Sites	TDN	DIN*	DON	TDN	DIN*	DON
River	48.73	4.44	44.29	31.33	9.08	22.25
Seagrass bed	21.10	3.18	17.92	19.60	1.23	18.37
Fishpen	20.54	3.05	17.48	22.84	3.35	19.49
Coral reef	13.17	3.65	9.52	12.73	1.86	10.86
Mangrove	18.00	3.74	14.26	33.44	9.71	23.73

Table 2. Percentage composition of DIN and DON in the five habitats during the dry and wet seasons

	Dry		Wet	
Sampling Sites	%DIN	DON	DIN	DON
River	9.55	90.45	25.84	74.16
Seagrass bed	16.25	83.75	6.89	93.11
Fishpen	14.96	85.04	13.22	86.78
Coral reef	32.31	67.69	15.47	84.53
Mangrove	22.71	77.29	29.08	70.92

9.71 µM during the dry and wet seasons, respectively. DON values ranged from 9.52 to 44.29 µM during dry season and 10.86 to 23.73 µM during wet season. DON concentrations were approximately 3-10 times higher than DIN during the dry season and 2 -15 times higher during the wet season. Mean DON concentrations in the coral reef area which were 9.52 µM and 10.86 µM during dry and wet seasons, respectively, were within the range of DON concentrations for tropical coral reef areas, at 3.0-13.8 µM as reported by Crossland (1983).

DON constituted about 70-90% of the total dissolved nitrogen in the five habitats in both seasons (Table 2). As reported by Jacinto (1992), about 90% of total dissolved nitrogen in the reef waters of Bolinao, Pangasinan is in the form of DON. The percentage of DON determined in the river sites (>70%) in both seasons agrees well with the results of Stepanauskas and Leonardson (1999) for organic N transported by river systems.

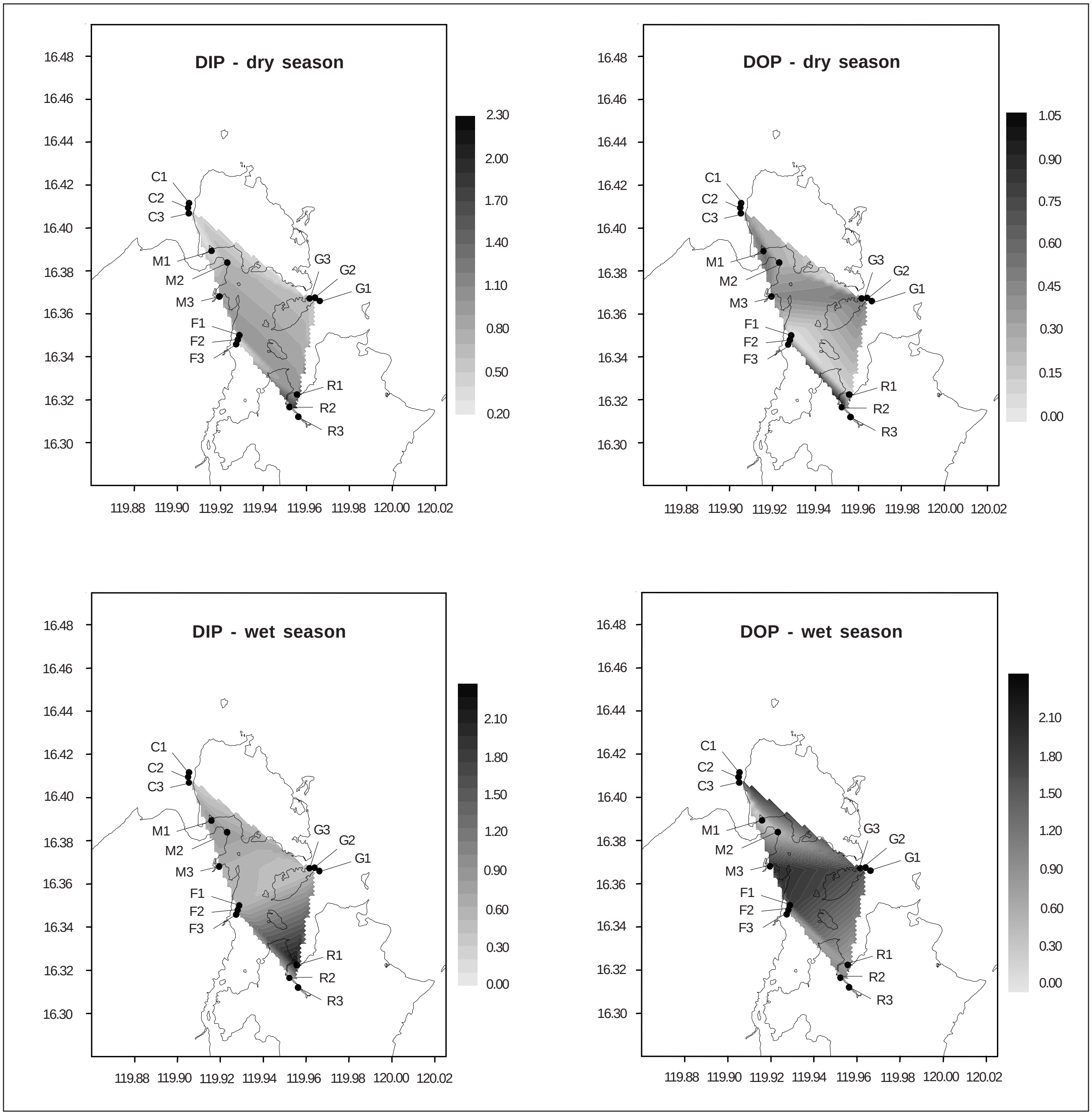

Fig. 4. Horizontal distribution of the phosphorous constituents during the dry and wet seasons

Phosphorus constituents

The horizontal distribution of the P constituents are shown in Fig. 4. DIP was highest in the river areas in both seasons and its concentration varied within the river system. This was not the observation in the other habitats. Higher DOP was observed during the wet season.

Fig. 5 shows the DIP and DOP concentrations in the five habitats. Highest DIP was measured in the river for both seasons; lowest DIP was measured in

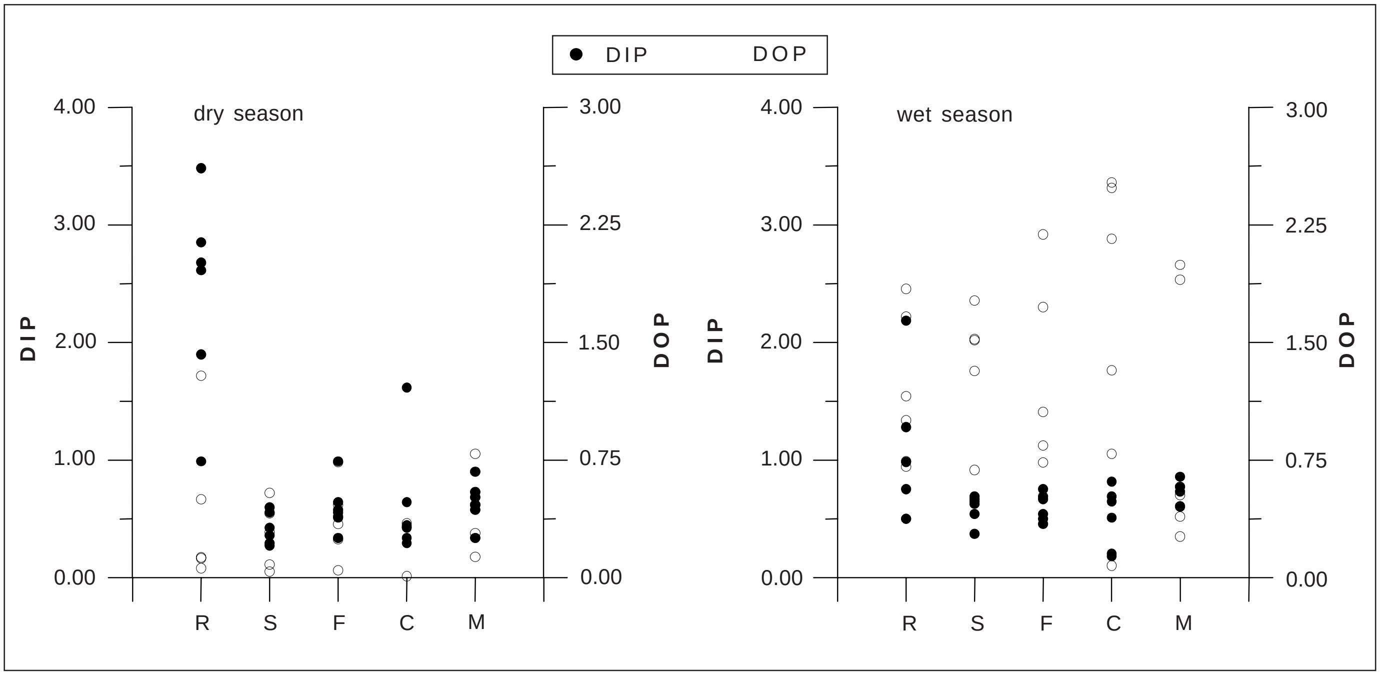

Fig. 5. DIP and DOP concentrations in the 5 habitats sampled: R = river, S = seagrass, F = fishpen, C = coral reef, M = mangrove, during the dry and wet seasons

the seagrass bed during the dry season, and in the coral reef area during the wet season. High DOP values prevailed in the river and mangrove areas, while low values characterized the coral reef area during the dry season. During the wet season, DOP was highest in the coral reef area and lowest in the mangrove area.During the wet season, higher DOP concentrations were observed in all habitats.

Concentrations of the P constituents are shown in Table 3. Except for the river system which had the highest DIP concentrations, DIP and DOP levels did not vary much within the 5 habitats during both seasons. DIP ranged from 0.42 to 2.71 µM during dry season and 0.51 to 1.03 µM during wet season; DOP ranged from 0.25 to 0.42 µM during dry season and 1.01 to 1.56 µM during wet season. Average DOP concentrations in the coral reef area (0.25 and 1.56 µM) obtained in this study were higher than that reported by Crossland (1983) for tropical coral reef areas (<0.15 µM). DOP constituted approximately 13-40% of the P constituents during the dry season and about 50-70% during the wet season. DIP constituted the greater portion of total dissolved P during the dry season (at 60-87%), but not during the wet season (at 30-50%, Table 4).

Table 3. Mean concentrations of the P constituents in the five habitats during the dry (May) and wet (August) seasons. (Values expressed in µM)

	Dry			Wet		
Sampling Sites	TDP	DIP (PO_4)	DOP	TDP	DIP (PO_4)	DOP
River	3.13	2.71	0.42	2.22	1.03	1.19
Seagrass bed	0.59	0.42	0.27	1.72	0.59	1.36
Fishpen	0.97	0.60	0.37	1.67	0.60	1.31
Coral reef	0.63	0.43	0.25	2.07	0.51	1.56
Mangrove	0.84	0.64	0.42	1.56	0.72	1.01

N/P ratio

Table 5 shows the calculated N/P ratio in each habitat. These were compared with the known Redfield ratio (N/P =16) which explains that major plant nutrients (i.e., NO_3, PO_4) change concentrations in seawater in a fixed ratio, that is, the same as the N and P stoichiometry of planktonic organisms (Redfield 1934, 1958). The inorganic N/P ratios in all the habitats sampled were lower than the Redfield ratio. The N/P value of 14, determined in the coral reef area, was highest among

Table 4. Percentage composition of DIP and DOP in the five habitats during dry and wet seasons

	Dry		Wet	
Sampling Sites	DIP	DOP	DIP	DOP
River	86.76	13.24	44.93	55.07
Seagrass bed	62.46	37.54	31.33	68.67
Fishpen	62.13	37.87	34.46	65.54
Coral reef	67.42	32.58	33.48	66.52
Mangrove	65.59	34.51	50.59	49.41

Table 5. N/P ratios in the five habitats during the dry and wet seasons

	Dry		Wet	
Sampling Sites	DIN/DIP	DON/DOP	DIN/DIP	DON/DOP
River	2.18	347.82	8.07	23.83
Seagrass bed	8.31	127.58	2.21	16.53
Fishpen	5.67	43.61	5.32	15.59
Coral reef	8.01	31.20	13.64	22.65
Mangrove	6.13	48.27	6.49	49.45

Table 6. Percentage compositions of N and P Constituents in the open ocean and coastal areas. * River data not included

Constituents	Open Ocean (Sulu Sea)	Coastal Area (Bolinao)	
		Wet	Dry
DON	42.49 - 74.89	70.92 - 93.11	67.69 - 90.45
DIN	25.11 - 57.71	6.89 - 29.08	9.55 - 32.3
DOP	16.66 - 29.39	49.13 - 68.67	34.41 - 37.87*
DIP	70.71 - 83.34	31.33 - 50.59	31.33 - 50.59

all habitats sampled. This value is greater than that reported for water flowing through the Eniwetok Atoll by Webb et al. (1975). The N/P ratios calculated from the organic fractions were relatively high because of the high DON, which was 2-15 times more than the DOP. The disparity in the DON and DOP values could also be due to the greater ease of converting the organic form of P to its inorganic form than the conversion of N. Organic P is readily hydrolysed to inorganic P, either by hydrolysis at the alkaline pH of seawater or by phosphatases, which are hydrolytic enzymes present in many bacteria and on the surface of some phytoplankton, particularly those from environments low in inorganic phosphate. In contrast, the conversion of organic N to its inorganic form is more difficult since its fixation, reduction and oxidation back to nitrate requires, the exchange of energy (Parsons and others 1984b).

Coastal area vs. open ocean

Table 6 compares the N and P constituents in the coastal area (Bolinao, Pangasinan) and in the open ocean (Sulu Sea). The percentages of DON (42-75%) and DOP (17-30%) in the open ocean were relatively lower compared to the coastal area. However, the difference was not significant because samples were collected in the upper 100 meters where production of organic matter occurred and regeneration or decomposition processes were not predominant. Nonetheless, the lower percentage of the organic forms of N and P in the open ocean was indicative of the efficiency of the system for nutrient recycling. From general knowledge of geochemical cycling, there is greater efficiency for nutrient recycling in the open ocean due to absence of proximity to possible sources as compared to the coastal area which receives inputs from various sources (rivers, land, etc.). The inorganic fractions of N and P were the dominant forms in the open ocean, while the organic forms of N and P were the dominant forms in the coastal area.

REFERENCES

Crossland CJ. 1983. Dissolved nutrients in coral reef waters. In: Barnes DJ, editor. Perspectives in Coral Reefs. Australia: Brian Clouston Publisher. p 56-68.

Jacinto GS. 1992. Is dissolved organic nitrogen (DON) more important than dissolved inorganic nitrogen (DIN) in tropical coastal waters [Abstract]. In: Chou LM, Wilkinson CR, editors. Third ASEAN Science and Technology Week Conference Proceedings, Vol. 6, Marine Science: Living Coastal Resources; 1992 Sept 21-23; Singapore. 219 p.

Jackson GA, Williams PM. 1985. Importance of dissolved organic nitrogen and phosphorus to biological nutrient cycling. Deep Sea Res 32(2): 223-235.

Koroleff F. 1983a. Determination of total phosphorus by acid persulphate oxidation. In: Grashoff K, Ehrhardt M, Kremling K, editors. Methods of seawater analysis. 2nd ed. Germany: Verlag Chemie. p 134-139.

Koroleff F. 1983b. Total and organic nitrogen. In: Grashoff K, Ehrhardt M, Kremling K, editors. Methods of seawater analysis. 2nd ed. Germany: Verlag Chemie. p 162-173.

Orrett K, Karl DM. 1987. Dissolved organic phosphorus production in surface seawaters. Limnol Oceanogr 32(2): 383-395.

Parsons TR, Maita Y, Lalli CM. 1984a. A Manual of Chemical and Biological Methods for Seawater Analysis. Oxford: Pergamon Press. p 3-25.

Parsons TR, Takahashi M, Hargrave B. 1984b. Biological Oceanographic Processes. 3rd ed. Oxford: Pergamon Press. p 164-166.

Redfield AC. 1934. On the proportions of organic derivations in sea water and their relation to the composition of plankton. In: James Johnstone Memorial Volume. Liverpool: Liverpool University Press. p 177-92.

Redfield AC. 1958. The biological control of chemical factors in the environment. Amer Sci 46: 205-221.

Stepanauskas R, Leonardson L. 1999. Bioavailability of wetland-derived DON to freshwater and marine bacterioplankton. Limnol Oceanogr 44(6): 1477-1485.

Webb KL, DuPaul WD, Wiebe W, Sottile W, Johannes RE. 1975. Enewetak (Eniwetok) Atoll: aspects of the nitrogen cycle on a coral reef. Limnol Oceanogr 20: 198-210.