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# Dynamics and elemental stoichiometry of carbon, nitrogen, and phosphorus in particulate and dissolved organic pools during a phytoplankton bloom induced by in situ iron enrichment in the western subarctic Pacific (SEEDS-II)

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ABSTRACT

The dynamics of organic carbon (C), nitrogen (N), and phosphorus (P) were examined during an in situ mesoscale iron-enrichment experiment in the western North Pacific in the summer of 2004. We separately determined the production of particulate organic matter (POM) and dissolved organic matter (DOM) and their subsequent removal during the bloom decline. As the iron-induced phytoplankton bloom progressed (days 0–14), POM increased in the surface mixed layer, while DOM did not increase significantly. The molar ratios for C:N, C:P, and N:P of the newly produced POM were estimated to be 4.9, 190, and 37 in the surface mixed layer, whereas the dissolved inorganic nitrogen to soluble reactive phosphorus drawdown ratio was 17. Preferential remineralization of P over C and N from the POM was postulated during the developing phytoplankton bloom. During the bloom decline (days 16–25), surface POM decreased with a similar C:N of 5.2. The N:P ratio of surface DOM increased during the bloom decline. Below the surface mixed layer, DOC and DON increased moderately after the peak of the bloom. The time-series variation of DOC and DON was not identical. The C, N, and P dynamics through the accumulation and removal of POM and DOM were complex. Grazing by mesozooplankton during the experiment may have played a significant role in the uncoupling of the dynamics of C, N, and P.


## 1. Introduction

Phytoplankton blooms in both coastal and open-ocean areas play a major role in the biogeochemical cycling of carbon (C), nitrogen (N), and phosphorus (P). Particulate organic matter (POM) produced by phytoplankton is transferred to higher trophic levels through the marine food web. A part of the organic materials is transformed into dissolved organic matter (DOM) by the direct extracellular release from phytoplankton, release of ingested prey organic matter by protozoan grazers, sloppy feeding by crustacean zooplankton, and cytolysis by viral infection (Nagata, 2000). Although sinking POM was considered to be the major removal process of organic matter from the surface (Eppley and Peterson, 1979), several studies have demonstrated that DOM also is an important component of the downward removal (Copin-Montégut and Avril, 1993; Carlson et al., 1994; Guo et al., 1995). Thus, partitioning of newly produced organic materials has been a matter of concern and has been studied by field observations and laboratory experiments (e.g., Biddanda and Benner, 1997; Carlson et al., 1998, 2000).

Loh and Bauer (2000) have reported complete data sets for distributions of C, N, and P in DOM and POM in the eastern North Pacific and the Southern Ocean. They showed that elemental ratios of DOM and POM are horizontally and vertically variable. Distributions of C, N, and P in POM (Copin-Montégut and Copin-Montégut, 1983) and DOM (Hopkinson et al., 1997) are also reported, but concurrent reports of C, N, and P in both POM and DOM are few. For the dynamics of POM and DOM during phytoplankton bloom events, the main focus was centered on C dynamics, and direct measurement of N and P are not available in the literature. Since C, N, and P have different cycling and turnover mechanisms, a concurrent and comprehensive study of C, N, and P in the production and decomposition of organic matter is required.

The North Pacific is one of the high-nitrate and low-chlorophyll (HNLC) regions (Harrison et al., 2004). Recent efforts for mesoscale in situ iron (Fe) enrichment experiments in these waters revealed that phytoplankton growth is limited by Fe

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availability (de Baar et al., 2005; Boyd et al., 2007). In summer 2004, the second in situ Fe-enrichment experiment in the western North Pacific (second Subarctic Pacific Iron Experiment for Ecosystem Dynamics Study (SEEDS-II)) was conducted to examine the Fe-induced phytoplankton bloom from the development through the decline (Tsuda et al., 2007). Dynamics of organic matter was one of the central themes of our interests in the in situ Fe-enrichment experiment. Although 12 in situ Fe-enrichment experiments were conducted between 1993 and 2005, data on the dynamics of DOC are available from only two experiments (Boyd et al., 2007). We need to accumulate data on a set of POM and DOM for understanding the dynamics of organic matter to Fe enrichment into the HNLC waters.

The present study explores the temporal dynamics of C, N, and P in both particulate and dissolved organic pools during an in situ Fe-enrichment experiment SEEDS-II in the western subarctic North Pacific.

## 2. Materials and methods

### 2.1. Description of experiment

A mesoscale in situ Fe-enrichment experiment (SEEDS-II) was conducted in the western subarctic gyre of the North Pacific (48.5°N, 165°E) in July–August 2004 by R/V Hakuho-Maru and R/V Kilo Moana (Tsuda et al., 2007). Dissolved Fe (332 kg of Fe as $FeSO_4$) and the inert tracer $SF_6$ were injected into the surface mixed layer over an area of $8\times8\,km^2$ from the R/V Hakuho-Maru on 20 July 2004 (denoted as day 0). The Fe infusion increased the in situ concentration of dissolved Fe from $<0.02$ to $1.4\,nmol\,L^{-1}$ (Nishioka et al., 2009). A second release of dissolved Fe (159 kg of Fe) without $SF_6$ was conducted onboard the R/V Hakuho-Maru in response to the declining dissolved Fe levels on 26 July 2004 (day 6), increasing the in situ concentration of dissolved Fe to $\sim0.7\,nmol\,L^{-1}$ (Nishioka et al., 2009). The Fe-enriched patch was tracked by elevated $SF_6$ (until day 12) or decreased $fCO_2$ (after day 12) for 25 days (Tsumune et al., 2009).

### 2.2. Sample collection

Seawater samplings were conducted inside (IN-patch) and outside (OUT-patch) the Fe-enriched patch. The positions of IN- and OUT-patch stations were determined as the center of the patch and outside the patch, respectively, by nighttime horizontal patch surveys (Tsumune et al., 2009). Since the samples collected from OUT-patch were not traced with $SF_6$, we mainly focus on the IN-patch data. Samplings were carried out aboard the R/V Hakuho-Maru during days 1–15 and 24–26, and by the R/V Kilo Moana during days 16–23. Discrete water samples were collected at predetermined depths (2, 5, 10, 20, 30, 40, 50, 75, 100, and 150 m) in 12-L Niskin-X and 10-L Niskin bottles attached to a CTD-carousel multiple sampler system on Hakuho-Maru and Kilo Moana, respectively. Subsamples were drawn from the Niskin bottles by gravity filtration through an in-line 47-mm Whatman GF/F filter (precombusted at 450 °C for 4 h), attached directly to the Niskin bottle's spigot. The filtered subsamples were collected for DOC, total dissolved nitrogen (TDN), and dissolved inorganic nitrogen (DIN) in precombusted (550 °C for 4 h) glass ampules and for dissolved P in acid-cleaned polypropylene bottles. The samples were stored at −20 °C until analysis. For particulate organic carbon (POC) and particulate nitrogen (PN) analysis, 2- and 1-L aliquots of subsamples from 7 depths (5, 10, 20, 30, 50, 75, and 100 m) were filtered through 47-mm precombusted GF/F filters onboard the Hakuho-Maru and 25-mm precombusted GF/F filters onboard the Kilo Moana, respectively, under gentle vacuum at $<0.01$ MPa. For particulate P (PP) analysis, subsamples (1–2-L aliquots) were taken from a single depth of 5 m and were filtered through a precombusted and acid-washed 25-mm GF/F filter under gentle vacuum. To prevent data scattering, only extremely large zooplankton (e.g., copepods) were removed from the filter sample for POM analysis using tweezers after washing with filtered seawater if they were captured on the filter during filtering the subsampled seawater. These filter samples were stored at −20 °C until analysis back in the on-shore laboratory. For chlorophyll *a* (Chl *a*) analysis, subsamples (112-mL aliquots) were filtered through 25-mm GF/F filter under gentle vacuum, and the filters extracted immediately with *N*,*N*-dimethylformamide at −20 °C in the dark over 24 h (Suzuki and Ishimaru, 1990).

### 2.3. Analytical methods

Dissolved organic C and TDN were measured simultaneously with a high-temperature combustion system (Ogawa et al., 1999), consisting of a total organic carbon analyzer TOC-5000 (Shimadzu) and a $NO_x$ analyzer ECL-880US (Yanaco). The outlet of the detector of the TOC-5000 was connected to the inlet of the ECL-880US. In this system, the non-dispersive infrared (TOC-5000) and the chemiluminescence detection (ECL-880US) were used for measuring $CO_2$ produced from DOC and nitrogen monoxide from TDN at a temperature of 680 °C. Filtered seawater samples were thawed in an ultra-sonicated water bath. Following the sample shaken by hand, the ample was opened, and the sample was acidified with 1% v/v of 6 N HCl. The sample was purged with high-purity zero $CO_2$ air for ca. 10 min, and then 100 μL of the sample were automatically injected into the combustion column. The analyses were done on a single sample, that was performed by typically four injections per samples and mean value was reported. The precision of replicate DOC measurements for a single sample typically was $\pm0.7\,\mu mol\,L^{-1}$ (ranging $\pm0.1$ to $1.4\,\mu mol\,L^{-1}$). The concentrations of DIN (nitrate plus nitrite (N+N), nitrite, and ammonium ($NH_4$)) were measured by standard colorimetric methods with a segmented flow autoanalyzer AACS-III (BRAN+LUEBBE). The DON concentrations were calculated by difference between TDN and DIN. The precision of the DON concentrations typically was $\pm0.11\,\mu mol\,L^{-1}$ (ranging $\pm0.01$ to $0.35\,\mu mol\,L^{-1}$).

Soluble reactive P (SRP) was measured by the molybdenum blue method (Hansen and Koroleff, 1999). Samples for total dissolved P (TDP) analysis were autoclaved in an acid potassium persulfate solution at 123 °C for 120 min (Ridal and Moore, 1990; Hansen and Koroleff, 1999). Total dissolved P concentrations were measured as SRP after removing excess free chlorine by placing the samples in a hot water bath for 2 h. The detection limits, given as three times the standard deviation of 10 blank measurements, for SRP and TDP were $0.01\,\mu mol\,L^{-1}$. Analyses for SRP and TDP were done on a single sample that was analyzed in triplicate, and the mean value was reported. The difference between TDP and SRP concentrations was assumed to be dissolved organic P (DOP). The precision of the DOP concentrations was typically $\pm0.02\,\mu mol\,L^{-1}$ (ranging $\pm0.00$ to $0.04\,\mu mol\,L^{-1}$).

Chlorophyll *a* concentrations were measured onboard with a fluorometer Model 10-AU (Turner Designs) with the non-acidification method of Welschmeyer (1994). Before POC and PN analysis, the filter samples were freeze-dried, and then exposed to HCl fumes for 4–5 h in a desiccator to remove inorganic carbon from the samples. Carbon and N contents on the filter were measured for single sample with a CN elemental analyzer EA1110 (Carlo Erba). The data for POC and PN contain an analytical error of up to 2.5%. Particulate P was measured as SRP after