3.3 Biogeochemical Responses

What have we learned regarding iron biogeochemistry from iron enrichment experiments?

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Several *in situ* iron fertilization experiments have been performed with the general goal to evaluate whether iron availability controls phytoplankton production in high nutrient, low chlorophyll (HNLC) waters of the equatorial Pacific (IronEx I, II) and Southern Ocean (SOIREE, EisenEx) (Martin *et al.*, 1994; Coale *et al.*, 1996; Boyd *et al.*, 2000, Gervais *et al.*, 2002). This hypothesis was also investigated in the western [**S**ubarctic Pacific Iron **E**xperiment for **E**cosystem **D**ynamics **S**tudy (SEEDS); Tsuda *et al.*, 2003)] and eastern [**S**ubarctic **E**cosystem **R**esponse to **I**ron **E**nrichment **S**tudy (SERIES); Boyd *et al.*, 2004] subarctic North Pacific using mesoscale iron infusions in order to enhance biological and geochemical signals. An *in situ* iron fertilization experiment is one useful approach to investigate oceanographic uncertainties and to aid in our understanding of iron chemistry, iron biology and the biogeochemical cycle of iron in seawater (Rue and Bruland, 1997; Gordon *et al.*, 1998; Bowie *et al.*, 2001; Croot *et al.*, 2001; Nishioka *et al.*, 2003; Wells *et al.*, 2003). In this report we have summarized "What have we learned regarding iron chemistry from previous *in situ* iron enrichment experiments?" and "What we still need to know".

Iron behavior after artificial iron release

Nishioka *et al.* (2003) and Wells (2003) investigated the changes in physical speciation of iron in an artificially iron-enriched seawater patch. These studies show that physical speciation was a useful method for studying iron behavior in seawater during a phytoplankton bloom.

After the artificial iron release, the bulk of the increased dissolved iron in the patch was colloidal and not truly soluble (Nishioka *et al.*, 2003; Wells 2003). The dissolved iron concentration decreased rapidly, with the loss rate gradually decreasing (Gordon *et al.*, 1998, Bowie *et al.*, 2001, Nishioka *et al.*, 2003; Wells 2003). However, the half-life of dissolved iron varied by experiment, which may be due to differences in physical conditions, such as temperature, mixing due to wind, and chemical conditions, such as ligand concentrations. This disappearance of the dissolved iron probably results from the colloidal iron aggregation and biological uptake of iron (Nishioka *et al.*, 2003; Wells 2003). Dissolved iron decreased to below natural conditions near the end of the bloom (Gordon e*t al.*, 1998; Bowie *et al.*, 2001; Nishioka *et al.*, 2003; Wells, 2003; Boyd *et al.*, 2004; Croot *et al.*, 2005). An exception was the retention of dissolved iron and ferrous iron (Fe(II)) after the final enrichment in **S**outhern **O**cean **I**ron **RE**lease **E**xperiment [SOIREE (Croot *et al.*, 2001)]. In the SEEDS experiment, we observed the colloidal iron transformation to particulate iron, with the latter being retained in the surface mixed layer (Nishioka *et al.*, 2003).

The above is an overview of our knowledge regarding the behavior of iron from previous experiments, but we still need more information about iron dynamics, such as the role of organic ligands in determining iron behavior.

Changes in iron bioavailability during a phytoplankton bloom

Wells (2003) reported biological uptake as being responsible for the disappearance of part of the soluble iron in the IronEx II study. In the IronEx II and SEEDS studies, a rapid depletion in the soluble iron fraction was observed during the phytoplankton bloom. However, this depletion in

soluble iron was insufficient to support the observed bloom development. Therefore, we have to consider an iron flux from another size-fraction to soluble iron species, such as a mechanism that allows some part of the colloidal iron to become bioavailable during a phytoplankton bloom (Nishioka *et al.*, 2003; Wells, 2003).

At the end of bloom, the Si:N consumption ratio increased and the F_v/F_m ratio decreased (Tsuda *et al.*, 2003; Wells, 2003; Boyd *et al.*, 2004) in the iron-enriched patch. These physiological changes indicate that diatoms underwent physiological iron stress after the bloom peak. At the same time, higher concentrations of particulate iron remained in the surface water in the SEEDS and SERIES patches than under natural conditions (Nishioka *et al.*, 2003; Johnson *et al.*, unpublished data). These results indicate that the bioavailability of the remaining particule and soluble iron was low. Therefore, the conversion of dissolved iron to particulate form will ultimately reduce the bioavailability of newly introduced iron into the photic zone.

We still need more information regarding changes in the iron bioavailability and the cycling of iron speciation in seawater to better understand how diatoms acquire various iron species.

Response of ligands production

Rue and Bruland (1997) found the concentrations of organic iron complexing ligands increased by 400% after iron infusion. Wells (2003) indicated that the bulk of iron ligand complexes were colloidal in size, and this feature of ligand production was also observed in the EisenEx study (Boye *et al.*, 2005) in the Southern Ocean. Croot *et al.* (2001) reported ligand concentrations increased at the end of SOIREE and the ligand concentrations had an affect on the dissolved iron concentration.

However, the source of organic ligands and their role in phytoplankton blooms is not yet fully understood. We are still not clear in regard to the process of iron ligand production.

What we still need to know

- *What controls iron retention and loss rate after iron release?*

Iron retention and loss rate after iron release may be controlled by physical and chemical conditions. We especially need to know more about chemical conditions, such as the role of organic ligands on iron concentrations and loss rates.

- *Response of ligand production to iron infusion, the main source of ligand production and the role of iron ligands in a phytoplankton bloom*

Although we observed an iron release-induced increase of organic ligands, the source of these ligands and their affinity for each iron species is not yet known. Furthermore, we still need to learn about the role of organic ligands in regard to iron dynamics and iron uptake by organisms during the phytoplankton bloom.

- *Changes in iron bioavailability during a phytoplankton bloom and how diatoms acquire iron species*

We still do not have enough knowledge regarding the bioavailable iron species in seawater. There may be complex interactions between the organic fraction and soluble, colloid and particle iron. We need to investigate these interactions for a better understanding of bioavailable iron fluxes to diatoms. This knowledge is very important in the understanding of how diatoms acquire iron species in seawater.

- *The role of Fe(II) in a phytoplankton bloom*

Croot *et al.* (2001) reported that there was a significant concentration of Fe(II) in the SOIREE and the EisenEx experiments (Croot *et al.*, 2005). The role of Fe(II) in a phytoplankton bloom immediately after the iron release might be important in understanding biological uptake. Redox and photochemical cycling will also influence iron chemistry.

- *Comparison with natural iron supply*

Lastly, we suggest the importance of comparing our knowledge of these *in situ* enrichment studies with the natural iron supply. The input of iron via *in situ* enrichment studies is very different from the natural iron supply, but the studies still contribute very useful knowledge towards our understanding

of the biogeochemistry of iron and its role in phytoplankton dynamics in HNLC regions.

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Iron dynamics and temporal changes of iron speciation in SERIES

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Over the past two decades, low iron values have been shown to be a major cause for limiting phytoplankton growth in large, macronutrient rich areas of the world's oceans. Iron enrichment experiments conducted in the Equatorial (IronEx I, Martin *et al*., 1994 and IronEx II, Coale *et al*., 1996) and the Southern Ocean (SOIREE, Boyd *et al*., 2000 and SOFeX) in regions of high nitrate, low chlorophyll (HNLC) have demonstrated increased productivity as a response to the added iron. However, the subarctic Pacific waters had not been investigated. In 2001, the first such subarctic experiment, the **S**ubarctic Pacific Iron **E**xperiment for the **E**cosystem **D**ynamics **S**tudy (SEEDS, Tsuda *et al*., 2003) was conducted in the Northwest Pacific with similar results. This was part of a plan that was conceived at the first meeting of the PICES Advisory Panel on *Iron Fertilisation Experiment in the subarctic Pacific Ocean* (October 2000, Tsukuba, Japan) where experiments were proposed in both the eastern and western Pacific. A collaborative project between Canada and Japan was proposed to study iron limitation in the subarctic Pacific, which has strong east–west zonal gradients in atmospheric iron deposition and plankton communities. Here, we describe the iron dynamics in the second subarctic experiment, SERIES (**S**ubarctic **E**cosystem **R**esponse to **I**ron **E**nrichment **S**tudy), near station P26 (station P, 50ºN, 145ºW) in the Northeast subarctic Pacific as the first field experiment of Canadian SOLAS (Surface Ocean Lower Atmosphere Study) funded jointly by NSERC (Natural Science and Engineering Research Council), CFCAS (Canadian Foundation for Climate and Atmospheric Sciences) and DFO (Department of Fisheries and Oceans).

The iron injection experiment was initiated at 0050 Pacific Daylight Savings Time (PDT) on July 9, 2002 at a site (50º 08.6′N, 144º 45.4′W) northeast of station P26, using an expanding square method made possible by the ship's (CCGS *John P. Tully*) Search and Rescue ECPINS® package. The release track covered an area of 4.75 × 4.74 nautical miles and was completed in 18 h travelling at a speed of ~ 4 knots. Two tanks filled with just under 10,000 L of seawater and acidified to a pH of 1.6 to 1.7 and each containing 1068 kilograms of iron sulphate heptahydrate per tank were mixed using swimming pool pumps (2 horsepower) and injected along with SF_6. This amount of iron was expected to give a 4-nM iron increase to ambient levels for a 65 km^2 patch of 30 m mixed depth. The injection area was actually 77 km^2 resulting in an addition of 90 moles of iron per square kilometre (or 90 $\mu mol/m^2$).

The first V-fin survey (Fig. 1) undertaken was 5.5 h after completion of the injection. The V-fin sampler was towed at approximately 2 to 3 m depth and the samples collected were analyzed primarily for dissolved iron. The concentration found was only 3 nM (3 $\mu mol\ m^{-3}$). Although this was close to our target of 4 nM, it was only a third of what we calculated due to the shallow 10-m thermal layer. Bowie *et al*. (2001) reported finding as much as 84% of the initial iron added in SOIREE in the dissolved phase. We only had one sample for total iron in the patch but since the dissolved iron was fairly well distributed (2.8 ± 0.3 nmol L^{-1}, n = 5), we feel we can use that total value as a good indication of the patch total iron concentration with some confidence (± 11%). The value determined was 8.6 nM, yielding an estimate of 86 mol km^{-2}. This estimate is within 5% of the calculated value for the iron addition and within the error of fluctuation of patch iron concentrations. Thus, approximately two thirds of the iron added was already associated with particulate matter.

A second survey 9 h later, or 17 h after the injection, found lower iron levels. The maximum dissolved iron was less than 80% of what we had found 9 h earlier and the total was only 60%. This was likely a result of the removal of iron via sinking particles as well as dilution of the iron patch both horizontally and vertically, with vertical dilution being stronger over this short time period.

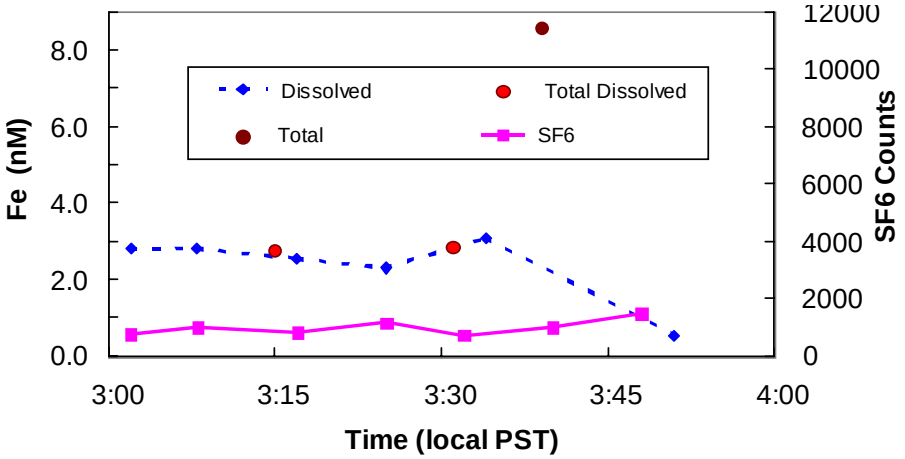

Fig. 1 Transect of iron in freshly injected patch, showing dissolved, total dissolved and total iron concentrations.

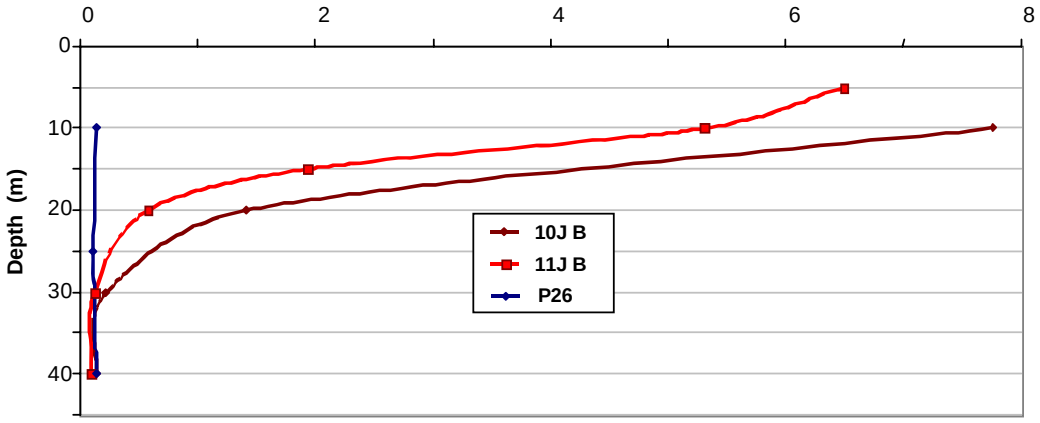

Fig. 2 Profiles of total iron for P26 prior to injection and for patch centre for the first 2 days (July 10 and 11) after injection.

The first profiles of iron (Fig. 2) collected 20 h after the injection shows iron to 20 m. The second profile (48 h) also shows iron below the 10 m thermal layer. If we integrate the iron in the water column over 20 m or 40 m (maximum sampling depth) we actually find more iron than that added (124 to 134 μmol m^{-2}) for total iron on July 10. This could be due to patchiness or due to the estimation of the iron concentration in the top 5 to 10 m. If we use the value from the V-fin survey just prior to the pumping profile, we reduce the estimate of integrated iron by 20 μmol m^{-2}. Even then the values for July 10 are still high (116 μmol m^{-2}). On July 11 the iron concentration was at the expected level (90 μmol m^{-2}) but about 20% less than the previous day. July 12 was almost identical to July 11, except for a lower surface value.

A change in the weather from calm to windy then mixed the water column down to 31 m. At this time there was even a trace of iron at 40 m, so that some iron was now sinking out of the patch and our sample area. The iron in the water column was constantly decreasing as is shown in the 10 m time line (Fig. 3). By July 15 (Day 6) surface dissolved iron was down to 0.4 nM (87% reduction) and the integrated total iron was 52 μmol m^{-2} (a 42% reduction). Because of the low surface dissolved iron, a second injection was undertaken. The iron was added only where we could detect SF_6 in more of a rectangular pattern as the patch had stretched in a north–south direction. The addition was calculated to give an increase of 19.7 μmol m^{-2} for a 92 km^2 patch. In this case, we found only 81% of the expected iron increase (*i.e.*, 16 μmol m^{-2} versus

19.7 µmol m^{-2} added) in our first sampling after the second release. The increase was relatively minor as the dissolved iron concentration increased from 0.4 nM to 0.6 nM and the total iron from 1.8 nM to 2.4 nM in the 10- to 20-m surface waters. By July 20 (3 days after the second injection) dissolved iron was 0.2 nM in the upper 30 m, still an order of magnitude higher than levels found when we arrived in the area (0.02 nM dissolved iron for P26 surface waters). By the time the ship left, the dissolved iron had dropped to 0.07 nM (10 m, July 23). These values were approaching historical background levels (Nishioka *et al*., 2001) but were still higher than what we found when we arrived at station P26 for this experiment. Although the dissolved iron was becoming indistinguishable from surrounding waters, the labile iron and total iron, both of which include particulate iron, was still very much elevated in the patch (Fig. 4).

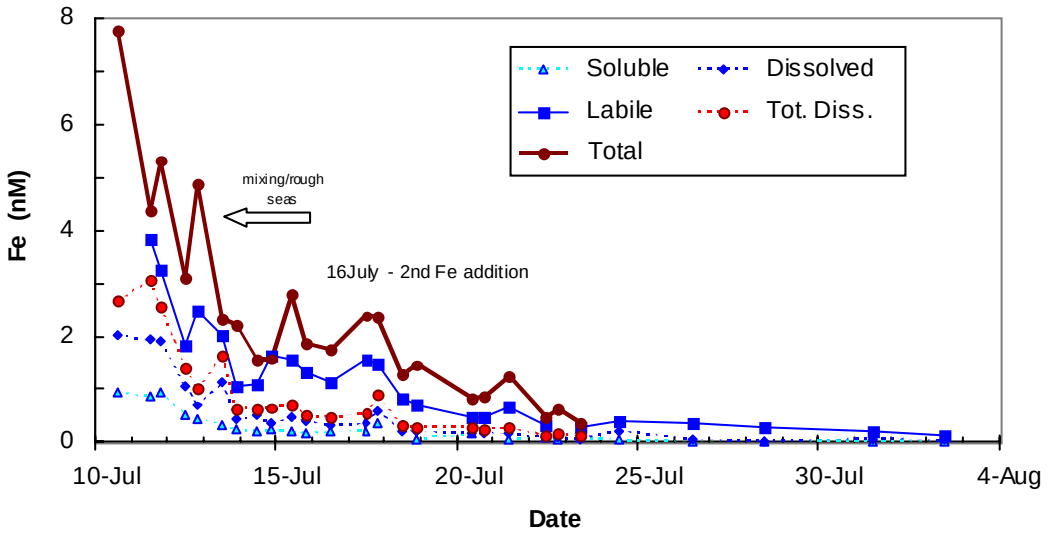

Fig. 3 Decline of 10 m surface iron over the entire experiment for all 5 measured iron phases.

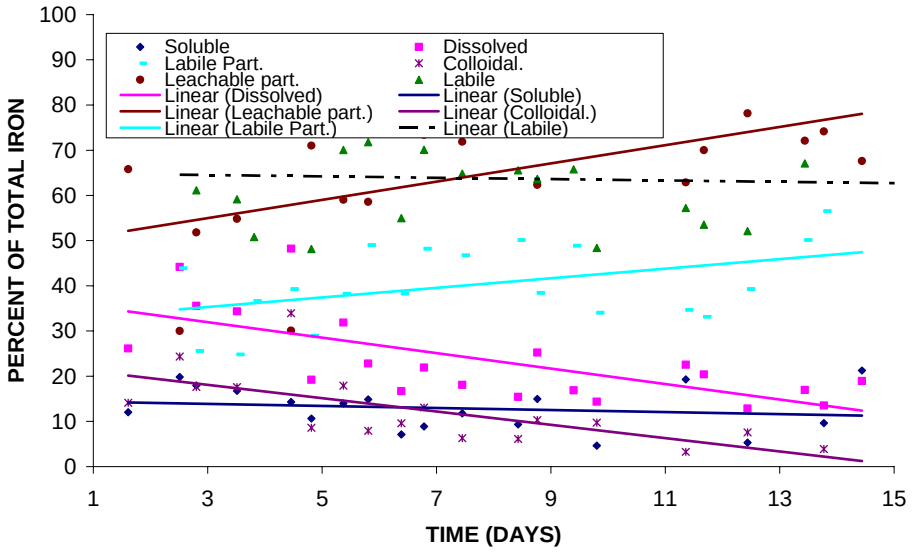

Fig. 4 Linear trends of percent of various iron phases (of total iron) over time using 10 m data

Iron budget

We also looked at the iron budget in the patch while taking into account horizontal expansion (Fig. 5). If we apply our integrated iron values for the centre of the patch and assume a relatively constant distribution throughout, we can assess how much iron is staying in the patch. This will be an over-estimation of the patch as the centre is not diluted as much as the edges but will allow us to estimate the iron loss over time. Further investigation of dilution as observed in SF_6 data should enable us to improve our estimates.

On the first sampling day (1.6) we found 150% of the added iron based on a volume of 99 km^2 (Cliff Law, pers. comm.) based on the assumption that the patch was completely homogeneous. This is at least a 50% overestimation of the total iron for a patch that had increased in area by 28%. If we adjust for this overestimation of iron and assign a value of 100% for Day 1.6, we find that as the patch increased over the next 2 days, we still had approximately 90% of the total iron in the patch. By Day 7 (just prior to the second injection) we still calculated almost 72% for total iron, or a 38% reduction from the first profile (Day 1.6). The second injection covered an area of 92 km^2 which is significantly less than the estimated area of the patch and therefore, makes budget calculation much more difficult but will be addressed in the future.

The other way to calculate the iron budget is to ignore the horizontal dilution, which was significant, and look only at the integrated iron of the patch centre. This will give us an underestimation of the iron remaining in the patch. Our first value was high, however, indicating that the patch was probably not homogeneous to start with or our calculation error is 20%. The day after the injection, we calculated more than 120% and by Day 6.8 prior to the second injection, almost 60% of the total iron was still accounted for in the top 40 m of the patch. From this we estimate the half life of the total iron in the patch to be approximately 6 days. Even by Day 11 we found 24% of the total iron in the centre station of the patch. When sediment trap data becomes available we will add this dimension to the results.

On the other hand, dissolved iron disappeared more rapidly. Using dissolved iron, we can only account for one third of the iron during our first sampling, if we assume it was all dissolved to begin with. It remained at this level for the first 2 days. Dissolved iron, based on patch centre station integration, dropped significantly to 12% on Day 3 and was only 10% by Day 6 prior to the second injection.

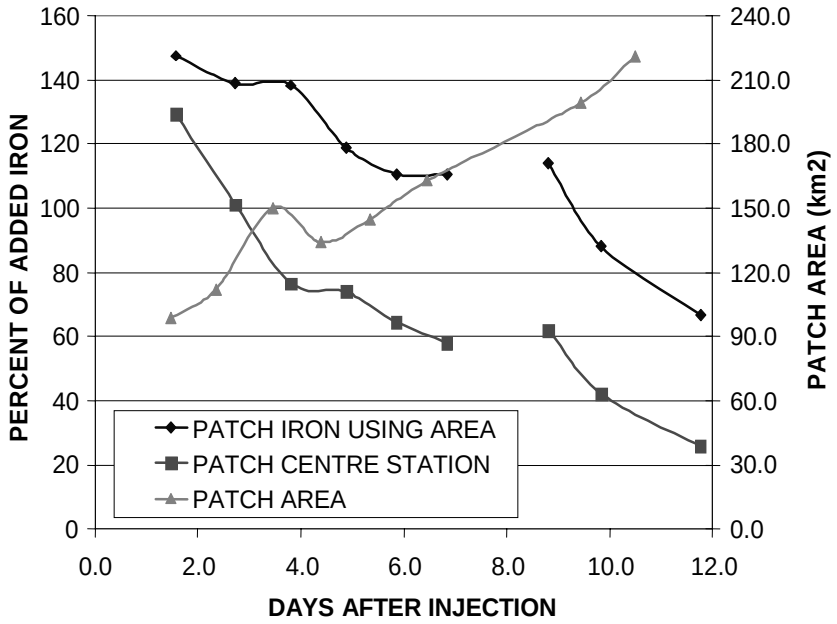

Fig. 5 Loss of integrated iron (0–40 m) as a percent of calculated iron added, with and without taking into account dilution due to patch spreading.

Summary

Only a third of the iron added to the patch was in the dissolved state after 8 h (first sampling). By Day 6 the dissolved iron, as measured in the water column at the centre of the patch, was only 10% of what was added but the total iron was still at 60%. The half life of the total iron was estimated to be 6 days. After 11 days we could still account for approximately 30% of the added iron. The iron appeared to be changing phases, with particulate iron increasing and colloidal iron decreasing.

The question remaining is what form of iron best indicates bioavailabilty? With this, we need to know uptake or consumption of iron for various organisms and how iron is recycled, and for the iron budget we need sediment trap data. Since we do not have good spatial coverage of the patch for iron, we need to use SF_6 values to determine the patch variations for iron content.

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Dissolved organic matter dynamics during SEEDS and SERIES experiments

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Introduction

Dissolved organic carbon (DOC) plays an important role in both stocks and flow of carbon in the ocean. Most of the organic carbon in seawater exists as DOC (Siegenthaler and Sarmiento, 1993). The pool of DOC is estimated to be 700 Gt C, a value comparable to the mass of inorganic carbon in the atmosphere (Siegenthaler and Sarmiento, 1993). On the other hand, DOC has significance as a byproduct of biological productivity and as a substrate for heterotrophic bacterial growth (Carlson, 2002). We need more information about DOC dynamics for a better understanding of ocean carbon cycling.

Considering *in situ* iron enrichment experiments, the carbon budget is one of our greatest concerns. Although DOC is an important component in the carbon budget during the experiment, DOC dynamics has not been studied well in previous experiments. In the present study, we investigated the DOC dynamics during *in situ* iron enrichment experiments in the western and the eastern subarctic Pacific, using high precision analysis.

Materials and methods

In situ iron enrichment experiments were conducted in the western subarctic Pacific (**S**ubarctic Pacific Iron **E**xperiment for the **E**cosystem **D**ynamics **S**tudy, SEEDS; 48.5°N, 165°E) from July 18 to August 1, 2001 (Tsuda *et al.*, 2003; Fig. 1) and the eastern subarctic Pacific (**S**ubarctic **E**cosystem **R**esponse to **I**ron **E**nrichment **S**tudy, SERIES; 50°N, 145°W) from July 9 to August 4, 2002 (Boyd *et al.*, 2004; Fig. 1). Our investigations were conducted from Day 0 to Day 13 in SEEDS and from Day 15 to Day 26 in SERIES. Vertical seawater samples were taken both in the iron patch and outside of the patch with X-Niskin bottles suspended on a Kevlar wire for DOC and chlorophyll (Chl-*a*) analysis. Niskin bottles equipped on CTD-CMS were used for taking particulate organic carbon (POC) samples. The samples for DOC were filtered through in-lined GF/F filters and preserved in glass ampoules at –20°C until analysis. The samples for POC were collected on GF/F filters which were kept frozen until analysis. For Chl-*a* analysis, seawater was filtered through a GF/F filter, and Chl-*a* was immediately extracted by solvent and analyzed on board.

The concentrations of DOC were measured (4 replicates for each sample) with a high temperature combustion instrument (Shimadzu TOC-5000; Ogawa and Ogura, 1992). The precision was ± 0.1 – 1.8 μM for SD or ± 0.1 – 3.1% for CV. The concentrations of POC were measured with EA1110 elemental analyzer (Carlo Erba).

Results

SEEDS experiment

A single 350-kg addition of iron as $FeSO_4$ over an 8 km by 10 km patch induced a diatom bloom during the SEEDS experiment. Chl-*a* concentration showed a rapid increase from Day 7 and approached 20 μg L^{-1} at the end of the

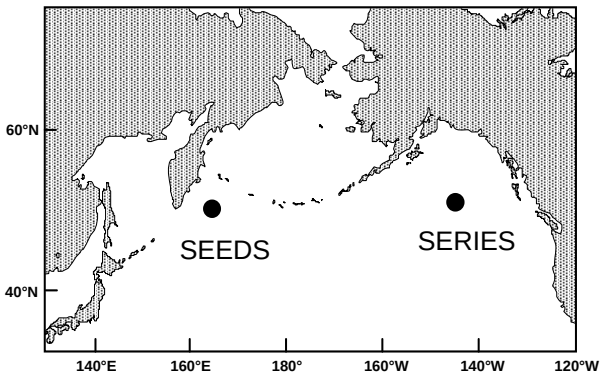

Fig. 1 Locations of *in situ* iron enrichment experiments in the western (SEEDS) and the eastern (SERIES) subarctic Pacific.

observation in the iron patch. Integrated Chl-*a* (0–20 m) increased from 15 mg m^{-2} on Day 0 to 302 mg m^{-2} on Day 13 (Fig. 2). Integrated POC also increased significantly after Day 7. The increase in Chl-*a* and POC was caused mainly by exponential growth of the chain-forming centric diatom *Chaetoceros debilis* (Tsuda *et al.*, 2003).

The concentration of DOC was about 60 μM on Day 0 and increased to more than 70 μM after Day 9 at the surface. Integrated DOC (0–20 m) increased from 1.2 mol m^{-2} on Day 0 to 1.3 mol m^{-2} on Day 13 (Fig. 2). Comparing the DOC values with those at Day 0, net DOC production at 0–20 m was estimated at 0.13 mol m^{-2} in our observation.

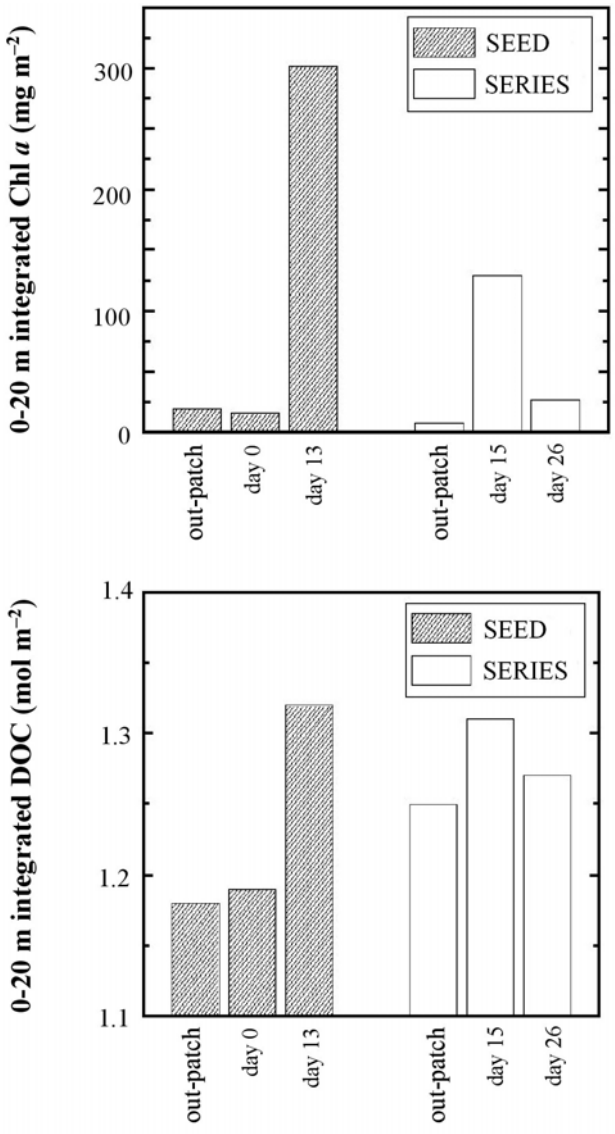

Fig. 2 Integrated values (0–20 m) for Chl-*a* (top) and DOC (bottom) during the SEEDS and SERIES experiments.

SERIES experiment

Double additions (at the beginning and at Day 6) of $FeSO_4$ over a 77 km^2 patch induced a diatom bloom which had a peak of 7–8 μg Chl-*a* L^{-1} around Day 15 (Boyd *et al.*, 2004). Our observations covered the stationary and the declining phase of the bloom. Integrated Chl-*a* (0–20 m) decreased during our observation, from 138 mg m^{-2} on Day 17 to 27 mg m^{-2} on Day 26 (Fig. 2).

On the other hand, DOC concentrations in the surface fluctuated between 65 and 72 μM during our observation in the iron patch. Comparing the DOC values in the patch with the mean DOC value out of the patch, the net DOC production was estimated at 0.02–0.10 mol m^{-2}.

Discussion

A significant portion of the organic carbon production was observed as DOC during the iron-induced diatom bloom in the subarctic Pacific. In the SEEDS experiment, 10–20% of net organic carbon production was converted into DOC. Significant DOC production was detected during the exponential growth phase of the phytoplankton bloom, although it is usually believed that DOC production occurred during the declining phase of the bloom (Norrman *et al.*, 1995; Wetz and Wheeler, 2003). In the SERIES experiment, DOC production was not always significant throughout our observation, although it was at the declining phase of the bloom in which the decomposition process seemed to dominate. However, if bacterial production was high during this period, DOC was likely to be decomposed as soon as it was produced.

On the other hand, what we still need to learn remain as open questions. The turnover time of the newly produced DOC is essential for estimating the amount of fixed carbon as a dissolved form by *in situ* iron enrichment. A decomposition experiment of DOC would supply useful information to calculate the DOC turnover time. Furthermore, the size spectrum of the newly produced dissolved organic matter is important for knowing the characteristics and bioavailability of DOC. Ultra-filtration is needed for this purpose. Finally, more effort should be made to elucidate the

mechanisms for DOC production in order to know DOC dynamics, not only for iron enrichment studies, but also for the ocean system. More knowledge of these issues will lead us to a better understanding of ocean carbon cycling.

Acknowledgements

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Formation of transparent exopolymer particles during the *in-situ* iron enrichment experiment in the western subarctic Pacific (SEEDS)

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Transparent exopolymer particles (TEP) formed from carbon-rich dissolved organic matter, assist sedimentation of organic matter out of the euphotic zone by forming a matrix of aggregated particles. The results of previous *in-situ* iron enrichment studies in the equatorial Pacific (IronEx I, II) and Southern Ocean (SOIREE, EsinEx) have been the generation of massive diatom blooms, but the subsequent export of fixed carbon to the deep layer has not been confirmed. Estimation of the organic matter flux, in terms of TEP in such enrichments, is an important biogeochemical criterion. Present work thus attempted to evaluate the enhancement of TEP formation and subsequent vertical flux of TEP during the *in-situ* iron enrichment experiment (SEEDS – **S**ubarctic Pacific Iron **E**xperiment for the **E**cosystem **D**ynamics **S**tudy) carried out in the western subarctic gyre in the North Pacific during July–August 2001.

A single release of 350 kg of iron as ferrous sulfate over an 8 × 10 km patch with a mixed layer depth of 10–15 m raised dissolved iron concentration from 0.05 nM to around 1.9 nM. Inside the iron-enriched patch, Chl-*a* concentration increased drastically from Day 7, reaching a peak concentration of 20 µg/L on Days 10 to 13. During the experimental period of 13 days, the time course of TEP concentration in the water column, as well as TEP flux in the sediment trap samples, were investigated. TEP concentration was quantified by the colorimetric alcian blue staining method of Passow and Alldredge (1995) and expressed in terms of xanthan gum (XG) equivalent.

Vertical profiles indicated higher TEP concentration in the upper 10 m, which gradually declined towards 70 m depth. TEP concentrations in the upper 10 m increased from 45–80 µg XG/L before the iron infusion to 190 µg XG/L on Day 13, which corresponds to those observed in the eutrophic coastal bays. The higher TEP in the surface mixed layer during Days 9 to 13 coincided with the stationary/senescent phase of the bloom when dissolved organic carbon (DOC) was released in higher concentration. In the initial period of the experiment, integrated values of TEP in the 5- to 20-m layer were consistently lower than those in the 20- to 70-m layer. However, when the bloom reached the peak, the 5- to 20-m and 20- to 70-m integrated amount in both layers was almost similar. Standing stock of TEP-C increased from 0.8 to 2.2 g C m^{-2}. Production of TEP-C by phytoplankton was around 260 mg TEP-C m^{-2} d^{-1} during Days 7 to 11. Accumulated TEP-C contributed about 16% to particulate organic carbon (POC) increase, and was equivalent to DOC increase. POC and DOC increased simultaneously with Chl-*a*, whereas TEP lagged by 2 days. A gradual increase in TEP below the mixed layer suggests that there is a lag in the downward flux of TEP.

TEP flux estimated from sediment trap samples varied from 41 to 88 mg XG m^{-2} d^{-1} and the contribution of TEP flux to the total mass flux was at a stable rate. Although the increase of TEP flux in the sediment trap, as the bloom progressed, confirms that TEP did sink out of the euphotic zone, a major part of the fixed carbon still remained in the surface mixed layer as particulate matter at the end of our observation. TEP concentrations were low compared to those expected from phytoplankton standing stocks, based on natural coastal bloom studies. A large diatom bloom observed in SEEDS did not aggregate, presumably because TEP production by the dominant diatoms was low.

The cycling of trace metals depends largely on the presence of TEP because of the high binding affinities of dissolved organic substances and trace elements to surface-active exopolymers. Trace metals adsorbed to TEP may be less available for phytoplankton growth. During SEEDS, dissolved iron concentrations subsequently decreased rapidly, and colloidal iron decreased most significantly

during the phytoplankton growth. While there was a high concentration of labile particulate iron (>0.22 μm), only a fraction was retained in the surface mixed layer at the end of the experiment. These results seem to imply the importance of acidic polysaccharides for the cycling of trace metals. TEP may have an influence on the residence time of iron (from atmospheric dust input) in the surface mixed layer, although the function of TEP as ligands for trace metals is not known yet. The role of TEP in the cycling of trace metals, especially iron and the bioavailability of iron bound to TEP, offers exciting future topics for research.

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Atmospheric measurement

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During the SEEDS-II cruise, the Atmospheric Chemistry Group is planning to measure the emission of biogenic gases from the surface of the enhanced primary production region fertilized by iron, to the atmosphere–ocean boundary layer (Fig. 1).

Our goals are consistent with those of the the Surface Ocean Low Atmosphere Study (SOLAS) Focus 1: Biogeochemical Interactions and Feedbacks between Ocean and Atmosphere.

Activity 1.1 Sea-salt Particle Formation and Transformations
Activity 1.2 Trace Gas Emissions and Photochemical Feedbacks
Activity 1.3 Dimethylsulphide and Climate
Activity 1.4 Iron and Marine Productivity

On the board of R/V *Hakuho Maru*, we have been preparing to measure chemical and physical parameters in the marine atmosphere shown in Figure 1. This is the first trial to measure atmospheric SF_6 which is emitted from the iron-enriched area in real time, developed by Y. Kajii and his group from Tokyo Metropolitan University (TMU). It is an indicator of emitted gases from the waters of the iron-enriched area associated with SF_6. Although the atmospheric components were not measured during the previous SEEDS cruise, some volatile organic substances in seawater, such as C_5H_8, increased in the iron patch area during the experiment. It was questioned that dimethyl sulphide (DMS) concentration in seawater did not show any difference between the 'in' and 'out' patch areas. For the SEEDS II cruise, the real time DMS measurements, both in seawater and atmosphere, will be carried out on the R/V *Hakuho Maru* and R/V *Kilo Moana*.

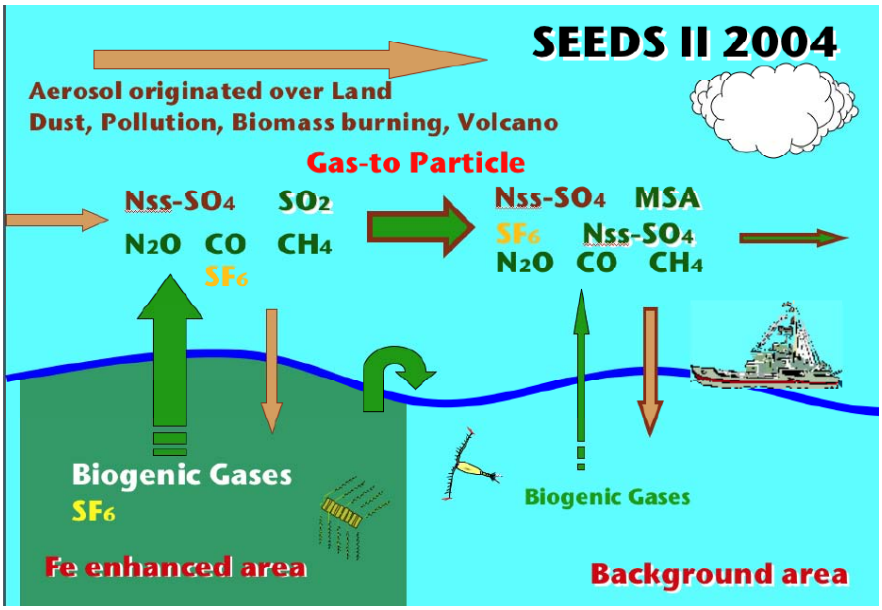

Fig. 1 Schematic image of atmospheric measurements during the SEEDS II cruise.

In addition to the aerosol samplings for the analysis of major and minor components and measurements of a number of concentrations for nano to micron particles with high time resolution (Mitsuo Uematsu: University of Tokyo and Kazuhiko Miura: Tokyo University of Science), frequent measurements for biogenic gases will carried out by following groups on the following ships:

R/V *Hakuho-Maru*

(1) DMS in seawater: Shinya Hashimoto, Shizuoka Prefecture University (SPU)
- DMS, DMSPd and DMSPp in eight samples will be obtained from the vertical profiles by using P&T-GC-FPD on a daily basis.
- Canadian SOLAS will measure the DMS turnover rate by using stable isotopes.

(2) DMS in air: Yoshizumi Kajii (TMU)
- They are developing a new analytical technique for DMS including isoprenes and other olefines by GC/FID/concentration. Besides DMS, SF_6, O_3, NO_x, SO_2, and CO will be measured continuously on board.

R/V *Kilo Moana*

(1) DMS in seawater and air: Ippei Nagao, Nagoya University (NU)
- DMS in both seawater and air will be analyzed simultaneously on board.

The intercomparison of atmospheric DMS concentration by TMU and NU, using the different techniques, was satisfied during the same cruise (Fig. 2). In addition, the air for DMS was sampled on a different deck level, which suggested that there was no pronounced vertical gradient of DMS for at least several meters, although the source of DMS is the sea surface.

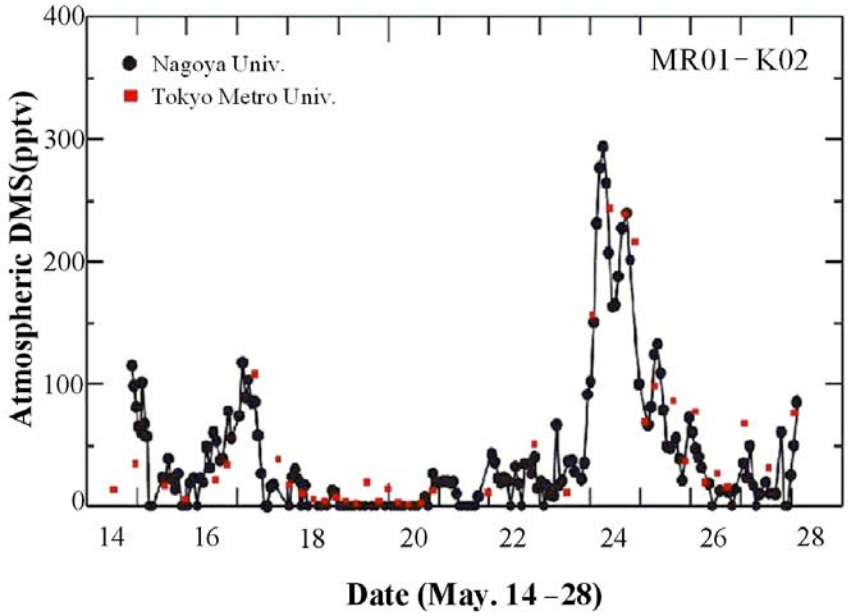

Fig. 2 Comparison of atmoshpheric DMS concentration during the R/V *Mirai* cruise. Data courtesy I. Nagao and Y. Kajii.

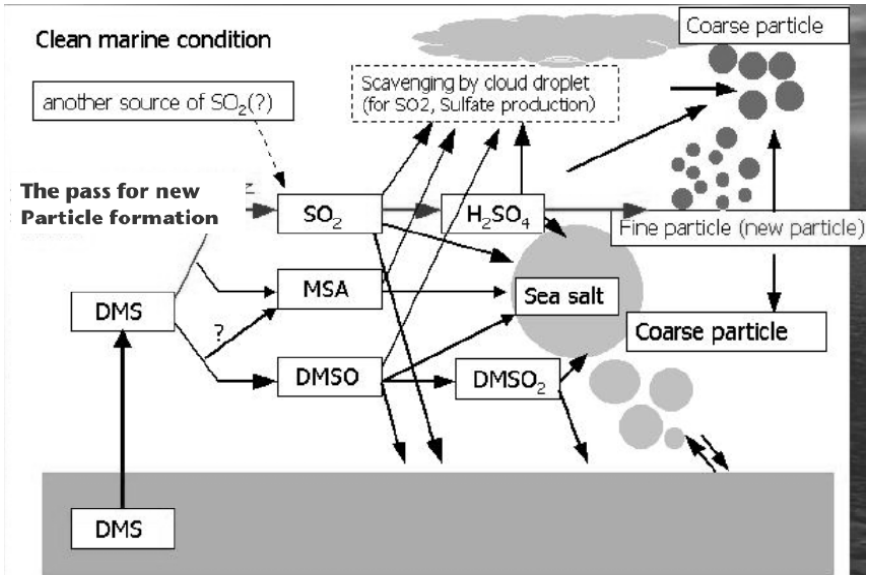

Fig. 3 Gas to particle transformation processes of DMS. Figure courtesy of I. Nagao.

The fate of atmospheric DMS shows various passes for scavenging from the atmosphere as shown in Figure 3. The efficiency of fine particle formation, which is expected to behave as direct radiative forcing from DMS is not known yet. It is important to observe the increase in nano particles produced from biogenic gases, that is, DMS, directly.

Atmospheric depositions of mineral dust (iron) and anthropogenic nitrogen compounds transported from the Asian continent may enhance marine biological activity. There will be a requirement to confirm that there is no obvious natural atmospheric input during the SEEDS II experiment.