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PICES Advisory Panel on *Iron Fertilization Experiment in the Subarctic Pacific Ocean*

Report of the 2004 Workshop on *In Situ* Iron Enrichment Experiments in the Eastern and Western Subarctic Pacific

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Edited by

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Foreword

Over twenty years ago, John Martin, Director of the Moss Landing Marine Laboratory, California State University, began putting evidence together from studies in the 1930s to propose that phytoplankton were limited by the availability of iron in some areas of the ocean. These regions were termed high-nutrient low-chlorophyll (HNLC) regions. Today, we know that the subarctic Pacific, equatorial Pacific, and the Southern Ocean are the three major HNLC regions of the world. Since Martin put forth his hypothesis, iron fertilization of HNLC water has been thought to be one possible approach to remove CO_2 from the atmosphere to combat global warming caused by greenhouse gases. Natural iron fertilization has also been hypothesized to control the glacial/interglacial shift in atmospheric CO_2.

The subarctic Pacific is characterized by a shallow (100–200 m) permanent pycnocline during winter, permitting relatively high numbers of phytoplankton and micro-grazers to subsist over winter. This, in turn, strongly influences the pelagic community structure. Two gyres, the Alaska Gyre (also called the Eastern Subarctic Gyre; both names used interchangeably in this report) and the Western Subarctic Gyre, dominate the subarctic Pacific. In the Alaska Gyre, Ocean Station Papa has produced a 50-year time series of physical, chemical and biological parameters, and has been the focus of three intensive sampling programs, the **SU**barctic **P**acific **E**cosystem **R**esearch Project (SUPER), the **W**orld **O**cean **C**irculation **E**xperiment (WOCE) and **C**anadian **J**oint **G**lobal **O**cean **F**lux **S**tudy (CJGOFS). In the Western Subarctic Gyre, the establishment of the time series station KNOT in 1998 has produced much data collected for understanding the seasonality of various parameters in this area.

In these two gyres, we now know that iron limits the utilization of nitrate and hence, the primary productivity of large cells, such as diatoms, except in the winter when iron and light may be co-limiting. In the Western Subarctic Gyre, which is in closer proximity to the Asia than the Alaska Gyre, the degree of iron limitation changes in parallel with the dust season in Asia. In fact, measured iron concentrations in the surface and deep waters seem to be higher in the Western Subarctic Gyre compared to the Alaska Gyre. Bottle incubation experiments have demonstrated that iron addition results in the increase in pennate diatoms in the Alaska Gyre and the increase in centric diatoms in the Western Subarctic Gyre. Such differences between these two gyres may also have an influence on the pelagic community structure and export production.

To test the iron limitation hypothesis of phytoplankton production in nutrient-rich areas of the open sea, iron fertilization experiments were first conducted in the equatorial Pacific under the programs IronEx I and II in the early and mid 1990s. These mesoscale enrichments experiments offered the chance to test the whole ecosystem response, and the results showed that iron supply controls phytoplankton processes, leading to enhanced phytoplankton stocks and associated macronutrient uptake and CO_2 drawdown. Another iron fertilization experiment soon followed in the Southern Ocean (SOIREE, **S**outhern **O**cean **I**ron **RE**lease **E**xperiment) during the summer season of 1999 and again demonstrated that iron supply controls phytoplankton growth and community composition, but the fate of produced organic carbon remains unknown.

The subarctic Pacific, with a unique water structure and biology, was the only HNLC region without an iron fertilization experiment to assess the iron hypothesis. Key questions that were not entirely resolved by the previous iron enrichment experiments, were:

1. How does the change in biodiversity and food-web structure differ for markedly different HNLC ecosystems which have been perturbed by an iron addition?
2. What is the drawdown of CO_2 and, especially, the flux of carbon to the deep ocean?
3. How does the production of ligands influence the iron chemistry and the longevity of the phytoplankton bloom?
4. How does zooplankton grazing influence the formation of the bloom and the carbon flux (*e.g.*, fecal pellet production)?

5. What is the long term response and recovery of the ecosystem following an iron addition?
6. What is the magnitude of production of other climate change gases, such as dimethyl sulphide (DMS) during the bloom, and how is the production influenced by phytoplankton species, microbial processes and grazing?

The proposal to establish an Advisory Panel on *Iron Fertilization Experiment in the subarctic Pacific Ocean* (IFEP-AP), under the BASS (BASin Studies) Task Team of the PICES Climate Change and Carrying Capacity (CCCC) Program, was approved at PICES VII in 1998, in Fairbanks, U.S.A. Working by correspondence, the Advisory Panel developed a workplan to tackle the following tasks: (1) to draw on the results of IronEx I, II and SOIREE to design a subarctic experiment and to come up with an hypothesis not answered in previous works; (2) to campaign for resources, particularly ship time required for successful experiments; and (3) to create an infra-structure for interaction, data distribution and publication, and scheduling for the participants.

A first IFEP-AP meeting was held at PICES VIII in October 1999, in Vladivostok, Russia. Here, the Advisory Panel (i) examined the reasoning for a subarctic iron experiment, the scale disciplines, and resources required to ensure success of the experiment, and (ii) produced a preliminary design of the experiment and its timing. The Panel provided an important co-ordination mechanism for international planning of meso-scale iron fertilization experiments conducted for the first time in the HNLC waters in the subarctic Pacific Ocean.

Japan organized the first of a series of experiments in the northwestern Pacific, SEEDS-I (**S**ubarctic Pacific Iron **E**xperiment for **E**cosystem **D**ynamics **S**tudy), in the summer of 2001, followed by the Canadian SERIES (**S**ubarctic **E**cosystem **R**esponse of **I**ron **E**nrichment **S**tudy) in the summer of 2002, in the northeastern Pacific, and the Japanese SEEDS-II in the summer of 2004, again, in the northwestern Pacific. The Panel also convened a series of international workshops (in October 2000 in Tsukuba, Japan, and in February 2004, in Victoria, Canada) so that international scientists engaging in iron fertilization experiments (*e.g.*, IronEx I, IronEx II in the equatorial Pacific, SOIREE in the subantarctic Pacific, and SOFeX in the Antarctic waters) could gather to share their experiences and exciting new findings, which came out as PICES literature as well as in publications in *Nature*, *Science*, and other professional journals. The Panel has served as a roadmap for the science of iron fertilization as a new tool for process research, and will point the way to future achievements.

This scientific report contains 13 extended abstracts by 25 participants from 3 countries involved in a PICES-sponsored workshop on "*In situ* iron enrichment experiments in the eastern and western subarctic Pacific", held February 11–13, 2004, in Victoria, Canada, which compares iron fertilization experiment results between the western and eastern subarctic Pacific. We have also provided background information that will enable the reader to refer to items and events related to this workshop. Appendix 1 includes the proceedings of the initial planning workshop on "Designing the iron fertilization experiment in the subarctic Pacific", held October 19–20, 2000, in Tsukuba, Japan, and co-sponsored by PICES and the Japan Central Research Institute of Electric Power Industry (CRIEPI). This workshop resulted in a spirited discussion among 39 participants from 5 countries and the submission of the extended abstracts from the 19 presentations. Appendix 2 is an historical list of all members of the Advisory Panel from 1999 to the present. Appendix 3 contains the IFEP-AP terms of reference, approved in 1999, and amended in 2004 to include a fourth term in response to the unexpected outcomes of the three iron enrichment experiments (SEEDS-I, 2001; SERIES, 2002, and SEEDS-II, 2004). Appendix 4 is comprised of the IFEP-AP Annual Reports, from its inception to 2004. The last Appendix contains featured articles on the iron enrichment experiments in the subarctic Pacific Ocean taken from the 2002 and 2004 issues of the PICES Press newsletter.

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PICES Advisory Panel on Iron Fertilization Experiment in the Subarctic Pacific Ocean

1 BACKGROUND AND OBJECTIVES

Iron deficiency has been proposed as the reason for the existence of surface waters rich in macronutrients but low in phytoplankton biomass in the subarctic Pacific, the equatorial Pacific and the Southern Ocean. In the summer of 2001, an iron enrichment experiment, the **S**ubarctic Pacific Iron **E**xperiment for **E**cosystem **D**ynamics **S**tudy (SEEDS-I), was performed in the western subarctic Pacific; in the summer of 2002, another iron enrichment experiment, the **S**ubarctic **E**cosystem **R**esponse to **I**ron **E**nrichment **S**tudy (SERIES), was carried out in the eastern subarctic Pacific (Fig. 1). These international collaborative projects between Canada and Japan were conceived at the first planning workshop of the PICES Advisory Panel on *Iron Fertilization Experiment in the subarctic Pacific Ocean* (IFEP), held in Tsukuba, Japan, in 2000, in conjunction with PICES IX (see Appendix 1 for details).

In order to review the results and outstanding questions from these experiments, and to discuss plans for a second, longer-term experiment in the western subarctic Pacific (SEEDS-II), a Workshop on "*In situ* iron enrichment experiments in the eastern and western subarctic Pacific" was held February 11–13, 2004, at the Chateau Victoria Hotel, Victoria, British Columbia, Canada. Twenty-six scientists from Canada, Japan, the United States of America, and the PICES Secretariat, attended the workshop.

The objectives of the workshop were to:

- Synthesize results from the two *in situ* iron enrichment experiments performed in the eastern and western subarctic Pacific (SEEDS-I and SERIES);
- Discuss responses to iron additions in lower and higher trophic levels, carbon cycles, trace-gas production and ocean–atmosphere flux, and models;
- Determine similarities and differences in biogeochemical and ecosystem responses to iron addition between the eastern and western subarctic Pacific;
- Identify specific scientific questions for the new longer-term experiment in the western subarctic Pacific (SEEDS-II).

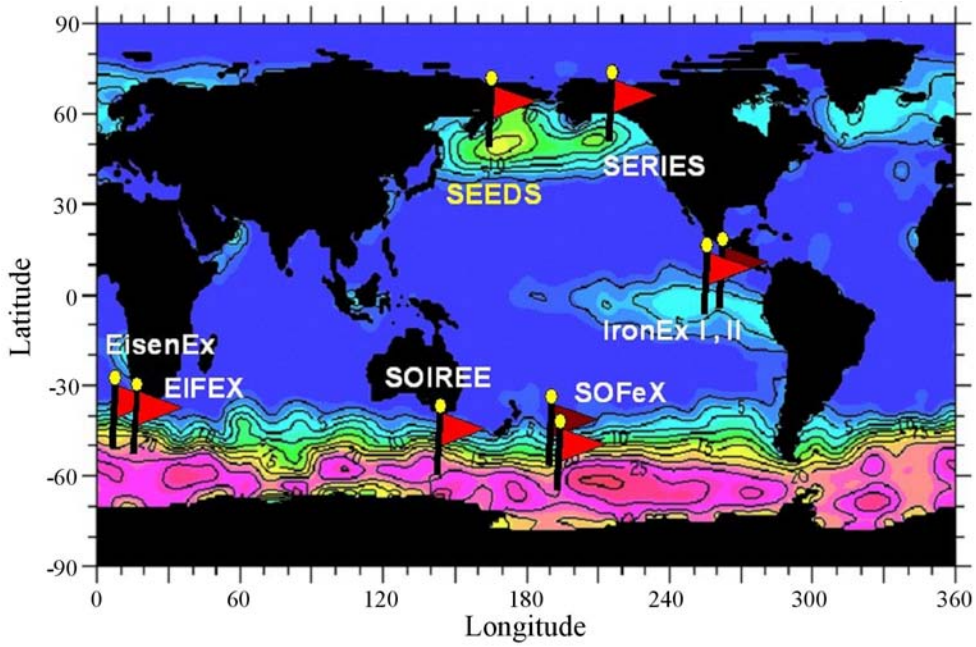

Fig. 1 Location of iron enrichment experiments in the Pacific and Southern Oceans (NOAA World Ocean Atlas, 1994).

2 2004 WORKSHOP SUMMARY

2.1 What have we learned from the enrichment experiments?

Fate of carbon

SEEDS-I

- There was no significant increase in export flux (13%), and the major part (75%) of the fixed carbon stayed in the surface;
- A significant portion of the organic carbon production was observed as dissolved organic carbon (DOC);
- Good agreement was found in DOC/Chl-*a* production ratio between SEEDS and SERIES;
- Transparent exopolymer particle (TEP) concentrations were low compared to phytoplankton standing stocks, presumably because TEP production by the dominant oceanic diatoms is low.

SERIES

- Eddies were an important influence on patch behaviour; drifter tracks tended to slip eastward relative to patch centres by wind stress;
- Intercalibration and sampling coverage between ships was good;
- Bloom evolution was captured in detail;
- Bloom decline – 80% of the particulate organic carbon (POC), fixed following iron enrichment, was no longer in the mixed layer by Day 25;
- Budgets could account for up to 70% of this POC (but using indirect methods) and 80% in N;
- Nanophytoplankton caused high particulate carbon on Days 7–10 of the bloom;
- What occurred after Day 20 to bring salt, NO_3, $Si[OH]_4$ and dissolved inorganic carbon (DIC) into the base of the patch? Is the simultaneous crash of the bloom a coincidence?
- What is the source of the high $CaCO_3$ fluxes to sediment traps?
- Between 50 and 125 m, biogenic silica dissolution was faster than organic matter decay. Can we believe this? Historical sediment trap and nutrient data suggest *yes*.
- Had bloom export terminated?
- An increase in DOC was not clear during the stationary and decline phases.

Ecosystem responses

SEEDS-I

- There were increases in Chl-*a* concentrations (× 26) and rate of primary production (× 13);
- A floristic shift to large cells (centric diatoms) was observed;
- Coastal diatoms responded quickly to the iron enrichment and built up a large biomass. So the presence of these coastal species as resting spores or cells are important factors for determining the time and magnitude of bloom evolution;
- Physiological stress by iron- and light-limitation was suggested after the development of the bloom;
- Enhancement of nitrate uptake rate (× 20) and marked consumption of macronutrients occurred;
- A large drawdown of pCO_2 was observed;
- Increase in bacterial abundance was × 2;
- Active heterotrophic dinoflagellates grazing on diatoms was observed after the development of the bloom;
- Gut-pigment contents of dominant copepods increased (× 4–18) but the absolute value was small;
- Picophytoplankton showed low growth rate before iron fertilization. Their growth rate was increased by iron fertilization. Quick responses in growth rate of picoeukariotes were observed on Day 2;
- Nanoheterotrophs showed a few days' delay to the increase in picoplankton growth, and grazing balanced picoplankton growth at the end of the experiment;
- Increase in grazing pressure on phytoplankton chain-forming *Chaetoceros debilis* by *Gyrodinium* sp. and *G. spilale* was observed during Days 9–13;
- Heterotrophic dinoflagellates (HDF) were the key grazers in SEEDS-I;
- Are larger HDF species abundant in the Western Subarctic Gyre compared with the eastern equatorial Pacific and the Southern Ocean?

- The contribution of HDF to the loss of diatoms in the surface mixed layer was significant during Days 9–13.

SERIES

- During phase II (Days 10–19) of the bloom, microplankton were dominant, comprising more than 80% of total Chl-*a*;
- There was a dynamic mixed layer ranging from less than 10 m to more than 40 m throughout the bloom, resulting in patch dilution;
- Dissolved iron concentrations were reduced to ambient levels by Day 12; F_v/F_m values suggest that phytoplankton were Fe stressed by Day 14;
- *Chaetoceros* spp. ceased increasing in abundance by Day 15, possibly due to iron stress;
- *Pseudo-nitzschi*a spp. maintained similar growth rates throughout the bloom, until SiO_3 concentrations were depleted;
- Although pennate diatoms dominated the bloom numerically with respect to carbon, both pennate and centric diatoms contributed equal proportions to algal biomass;
- The bloom peaked physiologically on ~July 21 (Day 12); this was the beginning of diatom iron stress;
- Primary production peaked on July 24 (Day 15); this was the beginning of diatom silicon stress;
- Chlorophyll peaked on July 27 (Day 18); after that, was the whole community beginning to suffer from iron limitation?
- Cells less than 20 μm increased from July 10 to 16 after which a major decline in coccolithophorids and other prymnesiophytes was observed;
- Susceptibility to photo-oxidation induced by the second iron addition(?)
- Microzooplankton: rapid response (abundance of flagellates and dinoflagellates increased from July 13);
- Grazing on diatoms might not be effectively carried out by abundant small copepods;
- *Eucalanus bungii* and *Neocalanus cristatus* were more effective diatom consumers but were in lower numbers;
- SERIES was not well matched with the spring period of maximum diatom grazing (*N. plumchrus*).

Iron biogeochemistry

SEEDS-I

- Increased dissolved iron was mainly in colloidal fraction;
- The dissolved iron concentration decreased rapidly, and loss rate gradually decreased;
- The half-life of initial dissolved iron was longer than that during IronEx and SOIREE;
- The disappearance of dissolved iron resulted from colloidal aggregation and/or iron biological uptake (less)
- Particulate iron remained at high levels;
- Bioavailability of the remaining iron (mainly particulate) was low;
- The character of organic ligands changed rapidly upon iron enrichment

SERIES

- Only 35% of the added iron was in a dissolved state after 8 h;
- The half-life of total iron was determined to be 6 days for an integrated water column of 0–40 m but 3 days for the 10 m depth concentration;
- If we also consider horizontal spreading, only half the total iron was still in the patch after 10 days;
- Colloidal iron % of total iron appeared to be decreasing while particulate iron increased;
- After 11 days there was still a considerable amount of iron left in the patch (~30%);
- Ligands seemed to track the dissolved iron concentration and seemed to disappear rapidly together with the dissolved iron concentration;
- Dissolved iron was near background level on July 22 (Day 13).

Trace-gas production, air–sea interaction

SEEDS-I

- There was no significant increase in dimethyl sulfide (DMS).

SERIES

- The iron enrichment created a bloom of DMSP-rich nanophytoplankton which crashed after July 20 (Day 11);

- Concentrations of particulate dimethyl-sulfoniopropionate (DMSPp) doubled during the nanophytoplankton (*Emiliana huxleyi*) bloom;
- The addition of iron created an overall DMS deficit of 7% in the mixed layer;
- The iron-induced increase in DMSPp had no clear effect on DMS concentrations, indicating that processes (*e.g.*, grazing) are more important than pool size;
- DMS concentrations were lower inside the patch during the peak of the diatom bloom;
- The iron-induced deficit in DMS concentrations during the peak of the diatom bloom resulted from a decrease in biological DMS net production.

Model studies

- A rapid response of microzooplankton grazing on small phytoplankton occurred;
- NH_4 buildup occurs after the bloom and stays in the subsurface layer up to early winter.

Similarity and differences between the eastern and western subarctic Pacific

Both SEEDS-I and SERIES have demonstrated increased productivity and biomass of phytoplankton as a response to the iron enrichment. Bloom evolution and decline were captured in detail during SERIES. However, there are differences in the physical and chemical environments, the plankton ecosystem and dominant species, and the zonal iron gradient between the Western Subarctic Gyre (WSG) and the Alaskan Gyre (AG). From SEEDS-I and SERIES, the following similarities and differences in biogeochemical and ecosystem responses to the iron addition were pointed out:

Similarities

- A diatom bloom occurred accompanied by a floristic shift to large cells;
- Vertically-integrated Chl-*a* and primary production increased;
- Heterotrophic dinoflagellates grazed on diatoms after the development of the bloom, which led to significant loss of diatoms in the mixed layer;
- Copepods were not the primary grazers; SERIES was not well matched with the spring period of maximum diatom (*Neocalanus plumchrus*) grazing;
- DOC increased during the growth phase of bloom, was constant through the stationary phase, and decreased during the bloom decline; DOC production was about 10% of primary production;
- Increased dissolved iron was mainly in colloidal fraction;
- Dissolved iron concentration decreased rapidly by colloidal aggregation and biological uptake (less), and loss rate gradually decreased;
- Particulate iron concentrations remained high; bioavailability of the remaining iron (mainly particulate) was low;
- The majority of macronutrients were consumed;
- An increase in Si/NO_3 drawdown ratio was observed after an occurrence of physiological stress, such as iron and light limitations.

Differences

- A larger and faster response (in terms of biomass) was observed in the WSG;
- Initial diatom populations were largely neritic for the WSG and pelagic for the AG; neritic species responded quickly to the iron enrichment and built up a large biomass, suggesting that the presence of coastal species as resting spores or cells is important in determining the magnitude of bloom evolution;
- The bloom was characterized by two ecological phases in SERIES. Phase I consisted of nanophytoplankton (prymnesiophytes) and occurred before Day 10 of the experiment; phase II was mainly diatoms and began after Day 10;
- Sediment traps collected large $CaCO_3$ fluxes after phase I, and high biogenic silica and POC fluxes after phase II during SERIES, but not in SEEDS-I. SEEDS-I occupation may have been too short to observe an export event;
- more than 50% of the mixed-layer POC deficit was attributed to bacterial re-mineralization and mesozooplankton grazing in the AG; NH_4 in surface waters increased throughout the bloom;
- Characteristics of organic ligands changed rapidly upon iron enrichment in the WSG; ligand concentrations tracked dissolved iron concentrations in the AG, rapidly disappearing together with the dissolved iron concentration;
- The iron enrichment created a bloom of

DMSP-rich nanophytoplankton (*Emiliania huxleyi*) which crashed after Day 11 in SERIES, but no significant increase in DMS/DMSP was observed in the WSG;
- The iron-induced increase in DMSPp had no clear effect on DMS concentrations in the AG;
- The iron-induced deficit in DMS concentrations during the peak of the diatom bloom resulted from a decrease in biological DMS net production in the AG.

Southern Ocean Iron Experiment

The Southern Ocean Iron Experiment (SOFeX) was performed in 2002 to investigate the effects of iron enrichment in regions with high and low concentrations of silicic acid. From the results of SOFeX, the following questions were identified to be resolved in future experiments.

- What are Fe:C:Si:N:P uptake and re-generation stoichiometries? How are these stoichiometries related to phytoplankton community structure? How do they change under macronutrient limitation (Si)? What are the spatial scales over which these elements are regenerated?
- What is the steady-state condition? Is this a relevant question?
- What is the periodicity and magnitude of natural iron enrichment, both seasonally and inter-annually, and on glacial–interglacial time scales?
- What is the effect of iron enrichment on the geochemistry (low O_2 and de-nitrification) and ecology (nitrification) below and within the iron patch?
- Do ecosystems respond in a natural manner to artificial iron enrichments? Effects on all biogeochemical parameters were well outside the contemporary climatological mean. What are the similarities and differences between natural and artificial iron supply?
- How important is NH_4 inhibition on NO_3 uptake and nutrient dynamics?

We need to rethink the effects of iron enrichment in low silicate and high nitrate environments, Si-limitation limited diatom growth in the North. We must address this issue as it bears directly on the significance for iron forcing of glacial–interglacial transitions and unintended consequences.

2.2 What are the outstanding questions?

SEEDS-II is the second meso-scale iron enrichment experiment in WSG designed to investigate the longer-term effects of iron enrichment on the plankton ecosystem, carbon export and trace gas production. SEEDS-II will involve about 50 researchers from universities and government institutions in Japan, the United States and Canada. The iron-enriched patch will be monitored by two ships, the R/V *Hakuho Maru* (Japan) and the R/V *Kilo Moana* (U.S.A.), for 34 days from July 21 to August 23, 2004. Through the integration and synthesis of the findings from SEEDS-I, SERIES and SOFeX, the workshop participants identified the following key themes and key scientific questions for the SEEDS-II experiment.

Fate of carbon

- What portions of organic carbon fixed by coastal centric diatoms in the WSG will be exported from the surface mixed layer, and what portions will be regenerated?
- To what extent would heterotrophic dinoflagellates (*Gyrodinium*) respire iron-induced carbon fixation?
- What is the turnover time, size spectrum, gross production rate, and gross decomposition rate of produced DOC?
- What are community respiration rates?
- Are C:N:P:Si regeneration ratios in surface and subsurface layers crucial to our understanding of iron-induced ecological response and nutrient dynamics?
- Is biological patchiness in species and export within the patch significant?
- How does physical dilution from outside affect the patch chemistry and biology? What is the effect of dilution on budget calculations?
- What is the difference between single and multiple iron additions? What is the difference in iron availability?
- To understand the fate of carbon during the iron fertilization-induced diatom bloom, studies on grazing rate, assimilation rate, and “mini pellets” sinking rates, are essential.

Ecosystem responses

- Why did SEEDS-I and SERIES have opposite trends in dominant diatom composition?
- What is the role of cell lysis on changes in available nutrients, sources of DMSP, bacterial community structure and iron chemistry?
- What roles will sinking and grazing play in the decline of the bloom?
- What is the long-term effect of iron availability on the ecosystem? How is the response to further iron addition affected?
- The ecological response to iron enrichment is largely determined by the seed population. What will the species variability and ecosystem differences be between iron-induced blooms in the same location?
- How predictable will the species response be to iron addition?
- Why does iron addition to bottles result in N limitation, but the large-scale iron additions show Si depletion?

Seasonal timing

- If natural events occur, should we try to emulate those that occur at other times of the year?
- What is the importance of the presence of endemic zooplankton at the time of iron enrichment?

Iron biogeochemistry

- What controls iron retention and loss after iron release?
- What is the main source of ligand production? How does it respond to iron enrichment?
- What is the role of iron ligands in iron bioavailability and recycling?
- What is the role of Fe(II) and redox-photochemical cycling in the phytoplankton bloom?
- What is the uptake of iron by different biota?
- What is the difference between single and multiple iron additions, and their effect on availability of iron?

- How different is the natural iron supply from the supply during the iron enrichment experiment? Labile particulate iron was significantly higher in the surface mixed layer in the WSG, but dissolved iron was at the same level as in the eastern region.
- Is bioavailability of iron (not total iron input) most important for ecosystem response?
- What form of iron best indicates bioavailability?
- What are the changes in iron bioavailability during phytoplankton bloom?
- Is there a significant iron supply by horizontal advection and winter vertical mixing in the western region? Supplied dissolved iron may be rapidly transformed to suspended particles during the phytoplankton bloom, and reduce bioavailability.
- To construct an iron budget, more detail is needed from vertical iron flux–sediment trap data, both horizontally and vertically, for a better understanding of the various forms of iron.
- Is there atmospheric deposition in these two different regions?
- How much iron do we need to add to get "the" ecosystem response?
- How different are export and recycling in "nature" versus bottle? Si versus N depletion?

Trace-gas production

- What is the fate of DMSP? Is it consumed by bacteria? Does it sink?
- What are the roles of physiological stress, Fe availability, light and macronutrients on DMSP cycling?
- What is the extent of emissions to the atmosphere?
- We need a consistent location (maybe tagged with SF_6) outstation for more reliable or consistent outsampling.

2.3 Recommendations for SEEDS-II

- It was recommended to lengthen the experiment if possible; the decline will depend on patch physical dynamics, bloom dynamics, *etc*.
- An additional suite of measurements is required to study bloom evolution, including fast repetition rate fluorometry (FRRF), flavodoxin, sinking rates, TEPS, and supplement these with ^{15}N and ^{32}Si uptake rates;
- Additional methods are required to determine the role of the microbial community and zooplankton in the fate of POC and O_2 profiles of the upper ocean, community respiration, labelled particle decomposition experiments;
- Additional experiments are required for measuring export flux, such as trap calibration with thorium, large-volume pump thorium samples, more fluorometers for the upper trap moorings;
- Estimates of silica dissolution, bacterial production and respiration (Bacterial C demand), and bacterial iron-stress should occur;
- Measurements of micro and mesozooplankton grazing on bacteria, phytoplankton, zooplankton and detritus are desirable;
- Biological patchiness in species and export within the patch should be considered;
- Response by changes in physiology of phytoplankton cells should be distinguished from that by changes in dominant species;
- Physical dilution from outside affects the patch chemistry and biology. The correction of dilution effects on budget calculations is essential;
- Intercalibration and data coverage between ships should be as robust as for SERIES.

3 EXTENDED ABSTRACTS OF THE 2004 WORKSHOP

3.1 Synthesis of the Iron Enrichment Experiments: SEEDS and SERIES

Iron fertilization experiment in the western subarctic Pacific (SEEDS)

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The **S**ubarctic Pacific Iron **E**xperiment for the **E**cosystem **D**ynamics **S**tudy (SEEDS) was conducted in the western subarctic Pacific (48.5°N, 165°E) from July 18 to August 1, 2001 (Fig. 1). The experiment consisted of a single addition of 350 kg iron as $FeSO_4$ with 0.48 M of an inert tracer gas sulphur hexafluoride, over an 8 × 10 km patch.

Concentrations of dissolved iron increased to 1.88 nM just after the iron injection, and subsequently decreased rapidly to 0.99 nM on Day 2. After this first rapid decreasing phase, the loss rate gradually decreased, and the iron concentration did not fall below about 0.15 nM, even after phytoplankton bloom development. The added iron stayed in the surface mixed layer in particulate form throughout the observation.

The first response of phytoplankton to iron input was observed on Day 2 as the increase in the photochemical quantum efficiencies of algal photosystem II (F_v/F_m) measurements of a fast repetition rate fluorometer. The increase in phytoplankton biomass became significant from Day 6 and exponentially increased to about 20 mg m^{-3} in chlorophyll-*a* concentrations until Day 10 (Fig. 2). After that, a relatively constant biomass of phytoplankton was observed from Day 9 to the end of the observation (Day 13).

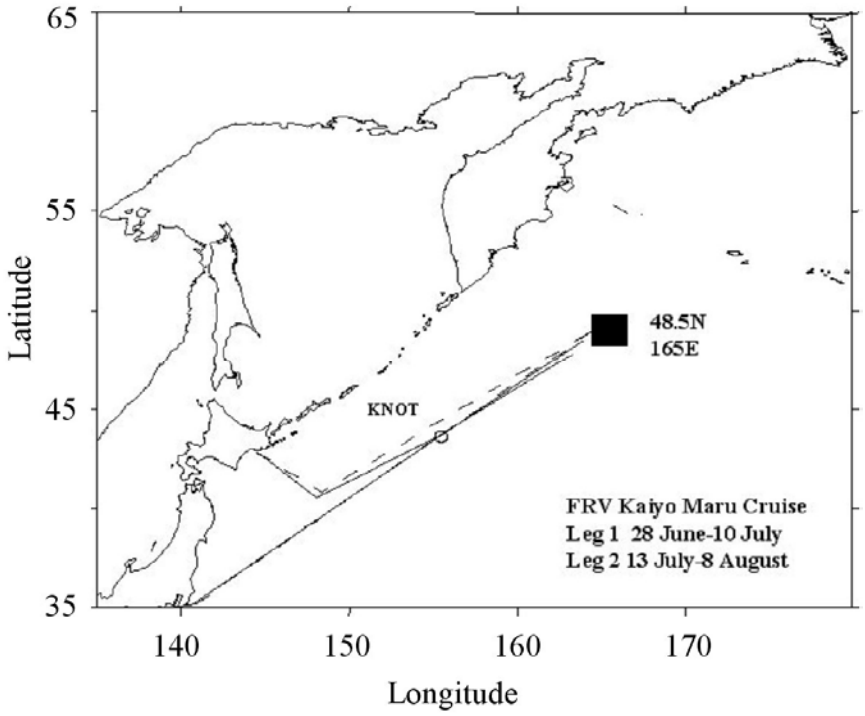

Fig. 1 Location of the iron enriched area of SEEDS, conducted in 2001, in the western subarctic Pacific.

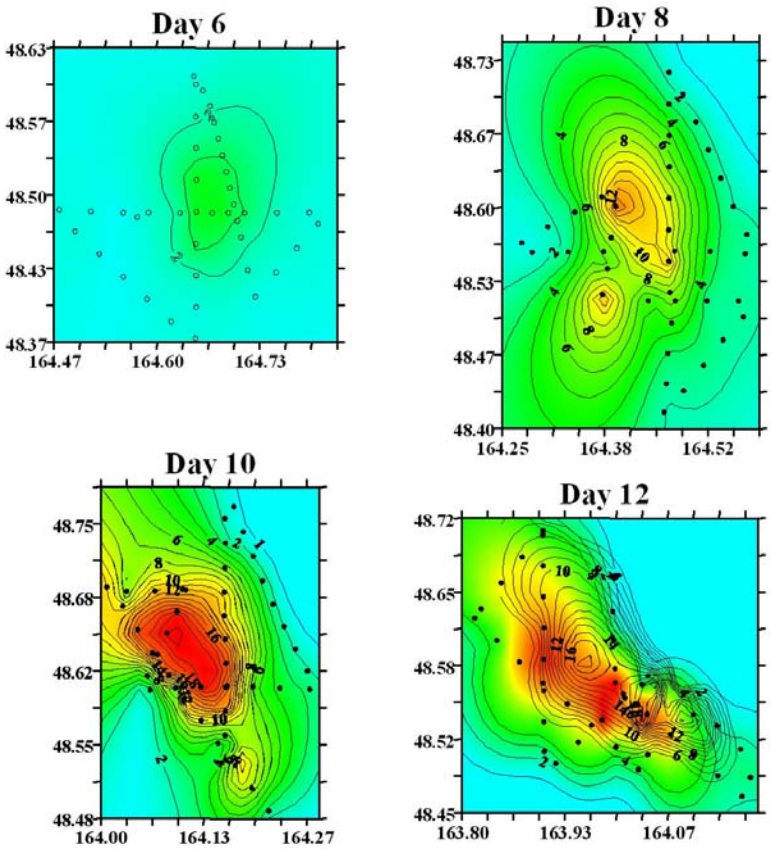

Fig. 2 Chlorophyll-*a* concentration in the surface layer of the iron-enriched patch during SEEDS.

In addition, the iron supply led to floristic shifts which resulted in the dominance of chain-forming, large centric diatoms. The fast growth and accumulation of large centric diatoms had not been observed in the earlier iron fertilization experiments conducted in the equatorial Pacific and the Southern Ocean. This large increase of phytoplankton standing stock was accompanied by large drawdowns of macronutrients, pCO_2, and dissolved inorganic carbon (DIC). Figure 3 shows that nitrate was abundant at 18 µM before the iron fertilization. The absolute nitrate uptake rate at 5 m depth sharply increased by 20 times after Day 7. The change of pCO_2 inside the iron patch was observed after Day 5. The maximum differences of pCO_2 and nitrate concentration in the surface water between inside and outside of the patch were 170 ppm and 11.7 µM, respectively, which were observed on Day 12.

High export flux of carbon in the patch was observed between Days 10 and 12 (Fig. 4). However, the export flux measured with drifting traps in the patch was not significantly different from that outside of the patch. The export flux between Day 2 and Day 13 was 12.6% of the integrated primary production in the patch. Moreover, the increase of particulate organic carbon (POC) content in the surface mixed layer was 78% of the decrease in DIC and influx of CO_2 from the sea surface. These results suggest that a major part of the fixed carbon still stayed in the surface mixed layer as particulate matter at the end of our observations. We were not able to determine, through lack of data, if the still-remaining organic matter had ultimately settled down, or decomposed in the mixed layer after our observations.

Highlights of this experiment have been published as Tsuda *et al.* (2003) and Nishioka *et al.* (2003), and other results have been published as 13 original papers in a special issue of *Progress in Oceanography* (2005, Volume **64**).

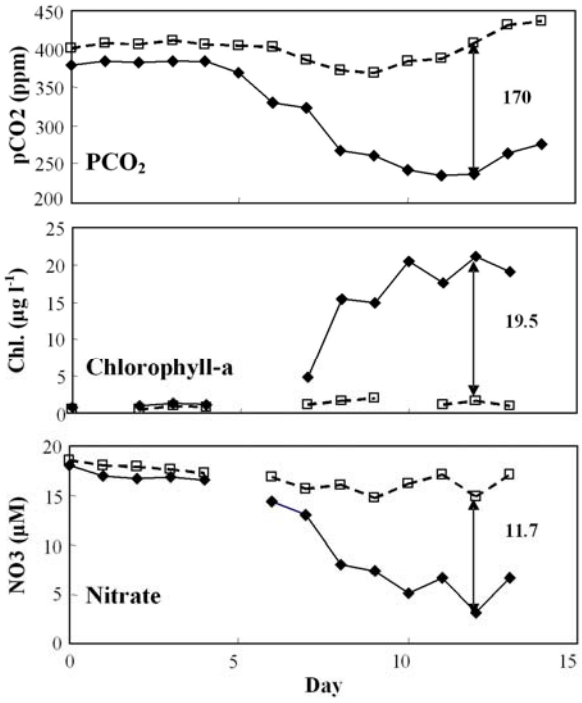

Fig. 3 Temporal changes of *p*CO2, chlorophyll-*a*, and nitrate concentrations at 5 m depth inside (filled symbols with solid lines) and outside (open symbols with broken lines) of the iron-enriched patch during the SEEDS.

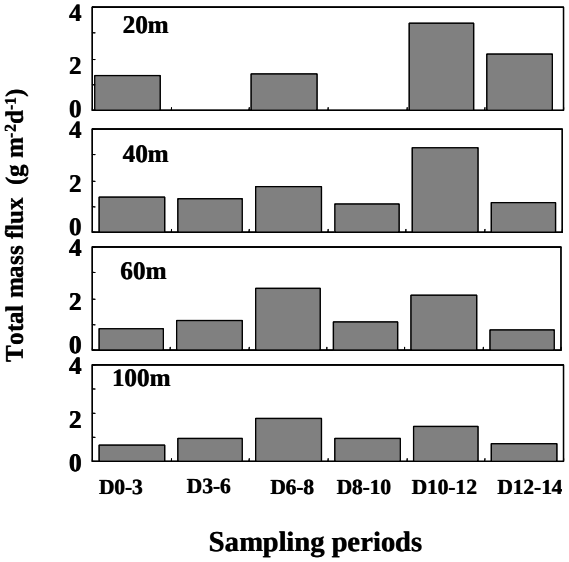

Fig. 4 Temporal changes of mass flux in the iron-enriched patch during SEEDS.

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The response of N and Si to iron enrichment in the Northeast Pacific Ocean: Results from SERIES

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Abstract

An iron enrichment experiment (**S**ubarctic **E**cosystem **R**esponse to **I**ron **E**nrichment **S**tudy), SERIES was carried out at Ocean Station Papa (50°N, 145°W) in the subarctic Northeast Pacific Ocean in July 2002, in order to observe the physiological, ecological and biogeochemical responses to a release from iron stress in these high-nitrate, low-chlorophyll (HNLC) waters. The patch was created by injecting $FeSO_4 \cdot 7H_2O$ (iron source) and SF_6 (water mass tracer) into the ship's wake while a Lagrangian grid of 8 km × 8 km was navigated. During the 27 days of occupation after iron release, the patch grew from < 100 km^2 to approximately 1000 km^2, and at Days 15–16 of the experiment, the patch shifted from a northward to an eastward drift, towards the centre of an eroded eddy. Shortly after, salinity and nutrient concentrations below ~10 m depth began to increase and, simultaneously (and possibly coincidentally), the iron-induced diatom bloom crashed. Mass balances of nitrogen and silicon were performed for two periods, separated at Day 20, when mixed-layer nutrient concentrations began to increase. Prior to Day 20, drawdown of silicic acid and nitrate was 13 μM and 5 μM, respectively, in the upper 30 m. $Si[OH]_4$ drawdown was balanced by biogenic silica (BSi) accumulation in the upper 50 m and sediment-trap flux at 50 m (export flux), while NO_3^- drawdown was balanced by the accumulation of particulate organic nitrogen (PON) and NH_4, and PON export flux. Because of the injection of nutrients below ~10 m after Day 20, nutrient drawdown was not observed for the latter part of the experiment, but there was a large decrease in BSi and PON concentrations in the upper 50 m. The decrease in BSi concentration was balanced by sediment-trap fluxes of BSi, but the decrease in PON concentration exceeded the sum of NH_4^+ accumulation and PON export flux. The imbalance in the nitrogen budget might be attributable to the poor constraint of changes in the dissolved organic nitrogen (DON) pool, or by the fact that dilution during patch growth has not been considered. These latter factors are the focus of on-going work.

Introduction

Over the past decade, mesoscale iron enrichment experiments have been performed to test the hypotheses that iron limits phytoplankton growth in HNLC regions of the world's oceans (*e.g.*, Gran, 1931; Martin and Fitzwater, 1988), and that greater wind-driven iron delivery to these regions during glacial periods resulted in higher primary production and organic carbon export, leading to the increased sequestration of carbon in deep oceanic waters and relatively low atmospheric CO_2 concentration during glacial times (Martin, 1990). All previous iron enrichment experiments have resulted in significant photosynthetic responses, and thus have demonstrated iron limitation in HNLC waters. However, bloom termination and export from the mixed layer have been observed only for the SERIES experiment. In some cases, the lack of such observations prior to SERIES is because physical conditions deteriorated the patch (IronEx I, EisenEx), but more generally the reason why the fate of iron-induced blooms had not been observed is because patch occupation had to be terminated before the end of the bloom (IronEx II, SOIREE, SOFeX north and south, SEEDS). During SERIES, the bloom crashed relatively quickly (by Day 20) and the drifting sediment-trap deployments caught much of the bloom export.

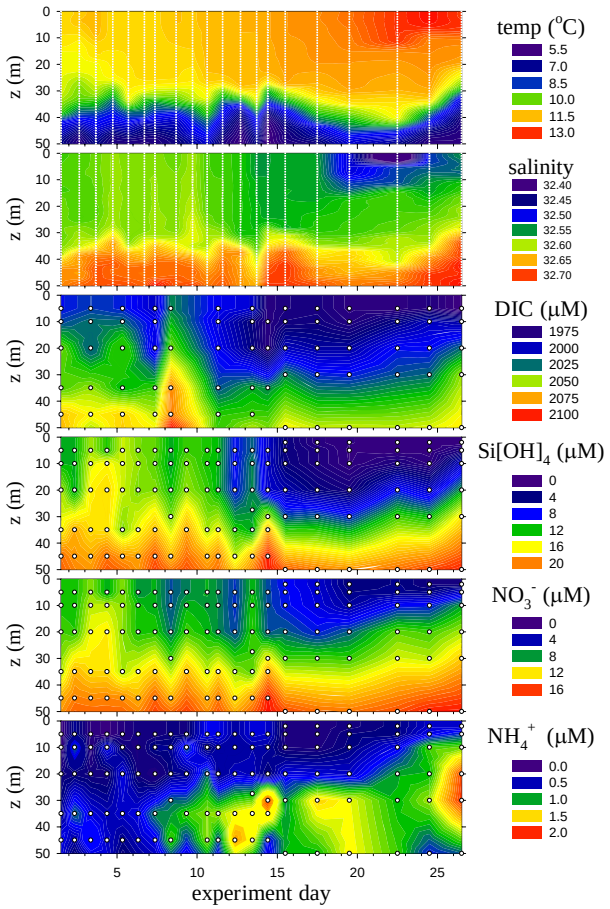

Fig. 1 Contour plots of temperature, salinity, dissolved inorganic carbon (DIC), $Si[OH]_4$, NO_3^- and ammonium (NH_4^+) for "IN" stations during SERIES. Sampling locations are denoted as points on the plots; T and S were collected at higher resolution (1 m) than for the nutrients (~10 m). Note high salinities between 10 and 30 m depth, beginning at Day 18, and the accompanying high nutrients.

Results and discussion

Several features of the iron patch are highlighted by the contour plots of Figure 1. In the upper 10 m, seasonal warming caused temperatures to increase. Salinity decreased as the patch migrated northeastward and surface nutrients (DIC, $Si[OH]_4$, NO_3^-) decreased throughout the occupation. However, beginning ~Day 18, relatively high salinity waters intruded into the patch below ~10 m bringing with them DIC, $Si[OH]_4$ and NO_3^- such that, integrated to 30 m depth, nutrient concentrations increased from Day 20 to the end of the occupation (not shown). Although these nutrient increases might be interpreted as a remineralisation signal, other evidence that they were advected into the patch with the high salinity waters is the increase in NO_3^- in the euphotic zone. Heterotrophic degradation oxidizes organic nitrogen to NH_4^+ which is then oxidized to NO_3^- by light-inhibited nitrifying bacteria, so that NH_4^+ oxidation occurs primarily below the euphotic zone. Here, NH_4^+ is used as a remineralisation signal.

For given time and depth intervals, mass balances account for changes in silicon and nitrogen for each pool in which these elements can be found. If changes in each pool are appropriately quantified, their sums should balance input and export of the elements from the volume of water being considered. Three events define the time periods of our mass-balance considerations. A mixing event occurred around Day 3, and led to the decision for a second iron addition, as the wind event resulted in low *in situ* iron concentrations. Period 1 (Tables 1 and 2) begins at Day 3. The shift from nutrient drawdown to nutrient accumulation at Day 20 marks the end of our period 1 and the beginning of period 2. The end of the occupation on Day 27 is the end of period 2.

There are two pools of silicon in the marine environment: dissolved $Si[OH]_4$ and particulate BSi. Within acceptable error, changes in these pools in the upper water column balance export fluxes of BSi for periods 1 and 2 (Table 1). $\Delta Si[OH]_4$ for the upper 50 m is ~25% greater than for the 30 m integral. Positive Si fluxes balance negative fluxes for both periods.

Table 1 Mass balance of silicon for experiment Days 3–20 (T_1) and 20–27 (T_2).

	$\Delta Si[OH]_4$	ΔBSi	BSi export
T_1	–390	240	130
T_2	0	–160	130

Note: All values are in mmol Si m^{-2} $period^{-1}$. $\Delta Si[OH]_4$ is for the upper 30 m, ΔBSi is for the upper 50 m, and BSi export is to sediment traps at 50 m depth.

Nitrogen mass balances are more complicated because this element resides in more pools than does silicon. The major nitrogen pools are NO_3^-, PON, dissolved organic N (DON) and NH_4^+. N_2 gas is by far the largest pool of nitrogen in seawater, but is assumed to have been biologically and

chemically unreactive during SERIES. The nitrogen budget during SERIES balances for period 1, but during period 2 the large loss of PON was not balanced by NH_4^+ accumulation and PON export (Table 2). ΔNO_3 for the upper 50 m is ~20% greater than for 30 m integral. Positive nitrogen fluxes balance negative fluxes for period 1, but not period 2. We are currently working on better quantification of the DON pool during SERIES, and results might improve the nitrogen balance for period 2.

Table 2 Mass balance of nitrogen for experiment Days 3–20 (T_1) and 20–27 (T_2).

	ΔNO_3	**ΔPON**	**ΔNH_4**	**ΔDON**	**PON export**
T_1	–160	39	24	45?	35
T_2	0	–82	26	???	22

Note: All values are mmol N m^{-2} $period^{-1}$. ΔNO_3^- is for the upper 30 m, ΔPON, ΔNH_4^+, and ΔDON are for the upper 50 m, and PON export is to sediment traps at 50 m depth.

Also, we have not quantified mixing with waters outside the patch. The general effect of mixing will be to make negative fluxes (nutrient uptake; Tables 1 and 2) more negative, and positive fluxes (particulate accumulation and export) more positive, so that consideration of mixing should not have a large effect on the balance of the budgets of Tables 1 and 2. However, better consideration of mixing will generate more accurate fluxes and may improve the balance of the budgets.

Summary

Iron enrichment in the subarctic Northeast Pacific (Ocean Station Papa) resulted in a significant photosynthetic response by iron-stressed phytoplankton. Nutrients (DIC, $Si[OH]_4$, NO_3^-) decreased throughout the bloom in the upper 10 m, but below 10 m depth began to increase after Day 18 due to the intrusion of a high-salinity water mass. Mass balances of nitrogen and silicon are generally good, but ongoing work will better quantify changes in the pool of dissolved organic nitrogen, and will account for mixing with waters outside the patch.

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3.2 Biological and Physiological Responses

Zooplankton responses during SEEDS

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During the **S**ubarctic Pacific Iron **E**xperiment for the **E**cosystem **D**ynamics **S**tudy (SEEDS), chlorophyll *a* concentration in the iron patch reached near maximum in 9 days (D9) after the iron fertilization and after that remained more or less constant. In spite of the stability of chlorophyll *a*, primary production was higher than 1.4–2.0 g C m^{-2} d^{-1} during D9–D13. As most of the carbon synthesized by phytoplankton after the iron fertilization (IF) was suspended in the water column (Tsuda *et al.*, 2003), these results indicated that loss by grazing, and other factors in the surface mixed layer during D9–D13, was as high as 3–4 mg chlorophyll *a* m^{-3} d^{-1}, assuming a C:Chl ratio of 30 and the mixed-layer depth of 15 m.

During the SEEDS experiment, heterotrophic nanoflagellates (HNF), microzooplankton, and macrozooplankton grazing rates were examined to understand the impact of zooplankton grazing pressure on phytoplankton dynamics and the carbon budget. Grazing rates of HNF and microzooplankton were examined by dilution experiments. Macrozooplankton grazing was measured by gut fluorescence method.

In the experimental site (in-patch), copepods *Neocalanus cristatus, N. plumchrus, Eucalanus bungii,* and *Metridia pacifica* were the dominant macrosized grazers. Gut pigment contents of copepods in-patch increased from D7–D8 and were 4 to 18 times higher than those outside of the iron patch (out-patch) during the peak bloom period (Tsuda *et al*., 2005). The community grazing rates in-patch were in the range between 2.4–10.2% of the daily primary production.

Prior to the IF, aloricate ciliates were the most dominant microzooplankton followed by heterotrophic dinoflagellates (Fig. 1). Tintinnids and copepod nauplii were relatively minor components. Aloricate ciliates gradually decreased after the IF. Heterotrophic dinoflagellates, dominated by *Gyrodinium* spp., increased rapidly after D9 and were the most dominant in the microzooplankton assemblage at the end of the experiment. The net growth rate reached 0.51 d^{-1} during D11–D13.

Grazing rates of microzooplankton decreased with the development of the diatom bloom until D9 (Fig. 2). On D11, the grazing rate abruptly increased. The net growth rates (gross grazing rate – grazing rate) of phytoplankton decreased after D11.

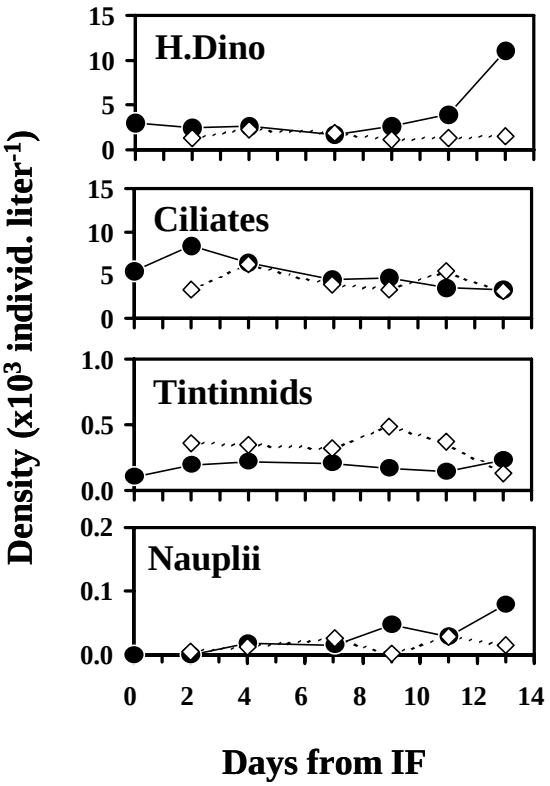

Fig. 1 Temporal change in abundance of microzooplankton (>10 μm) in the top 10 m of the water column. Filled and open symbols mean in-patch and out-patch, respectively.

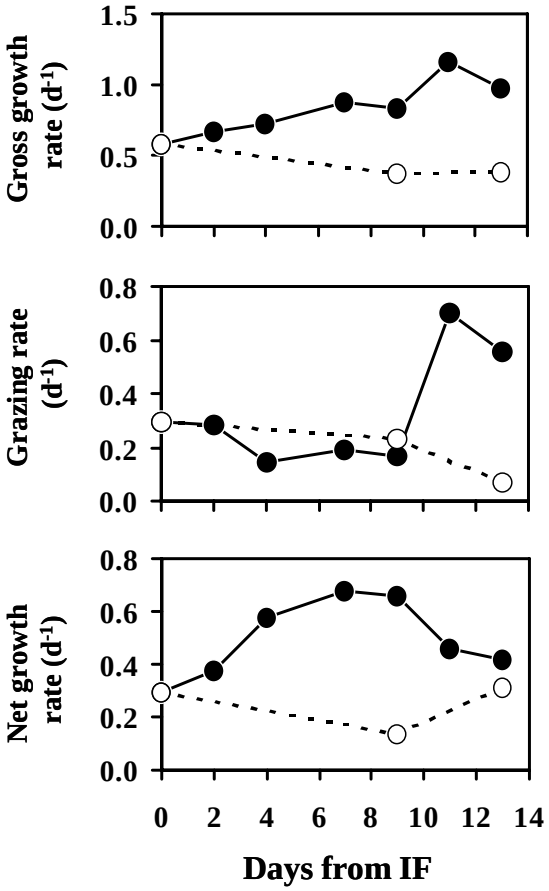

Fig. 2 Results of dilution experiments for total phytoplankton. Filled and open circles mean in-patch and out-patch, respectively.

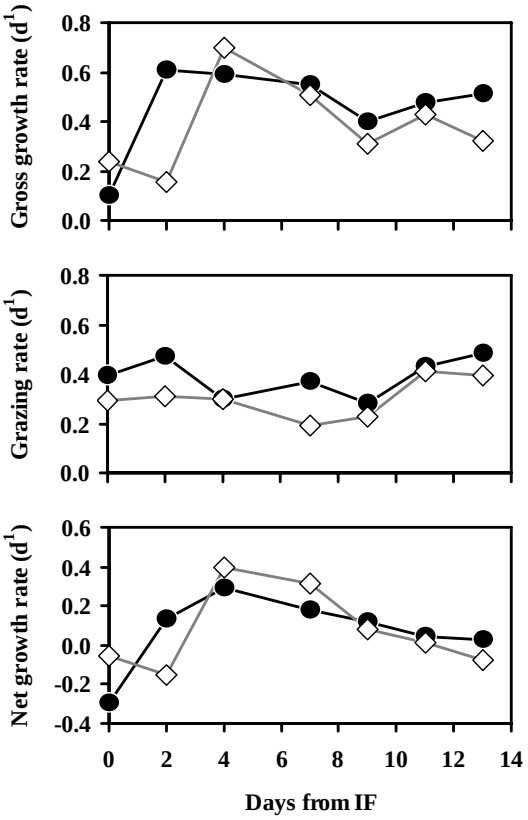

Fig. 3 Gross growth rates, grazing rate and net growth rates of eukaryotic ultraphytoplankton (filled circles) and cyanobacteria *Synechococcus* (open diamonds).

In phytoplankton smaller than *ca.* 5 μm ESD (equivalent spherical diameter), determined by flow cytometry analysis, eukaryotic ultraphytoplankton (EUKU) and cyanobacteria *Synechococcus* (SYN) predominated. Before the IF, gross growth rates of EUKU and SYN were 0.10 d^{-1} and 0.24 d^{-1}, respectively (Fig. 3). Gross growth rates of EUKU and SYN increased on D2 and D4, respectively, then gradually decreased. The grazing rates on EUKU and SYN decreased slightly with time, and increased again after D11. Net growth rates of EUKU and SYN increased after the IF and gradually decreased with time. At the end of the SEEDS experiment, growth and grazing mortality rates of ultraphytoplankton balanced each other.

Present results show that all the grazers increased their feeding activity after the IF but responses were variable. Increase in gross growth rate of ultraphytoplankton was the first biological response to the IF during SEEDS. The grazing rate of HNF on ultraphytoplankton did not increase rapidly and excess growth was observed. However, the relationship between growth and grazing returned to the original balanced one within 6–8 days. Results show that the relationship between growth rates and grazing mortality rates of ultraphytoplankton had a relatively strong convergent potential to balance each other against environmental perturbation.

Grazing by heterotrophic dinoflagellates was an important loss factor of phytoplankton at the later part of SEEDS, and they might have played an important role in keeping cholorophyll *a* concentration steady after D11. In general, chain-forming diatoms like *Pseudonitzschia pungens* and *Chaetoceros debilis* are too large to be prey for microzooplankton. However, it is known

that some heterotrophic dinoflagellates can feed on prey larger than themselves (*e.g.*, Jacobson and Anderson, 1986). Light and scanning electron microscope studies showed that *Gyrodinium* spp. contained diatom cells. The biology and ecology of *Gyrodinium* spp. in the subarctic Pacific (*e.g.*, distribution, feeding rate, feeding behavior, growth rate, fecal pellet production rate, elemental composition of feces, *etc.*) are not well understood. Further studies are needed to understand the role of *Gyrodinium* spp. on phytoplankton dynamics and the fate of carbon synthesized during the diatom bloom induced by IF.

Although the response of copepods to the increase in prey phytoplankton was quite obvious, their grazing influenced only slightly the phytoplankton dynamics within the 13-day SEEDS experiment. This was due to the slow growth rate of copepods compared to microzooplankton and HNF. Saito *et al.* (2002) showed that the copepod grazing influence was insignificant at the peak phase of the diatom bloom in the Oyashio region, but it was an important loss factor of phytoplankton after nutrient depletion. This suggests that the fate of carbon synthesized during the IF-induced bloom would be influenced by copepod grazing after nutrient depletion as well as by *Gyrodinium* grazing.

One of the important pieces of information obtained by SEEDS is that relatively minor components in the food-web functional group prior to the IF became key players after the IF. *Chaetoceros debilis* was a negligible component in the phytoplankton assemblage prior to the IF but increased abruptly after the IF and was the most dominate. The most significant response of grazers to the outburst of *C. debilis* was by a relatively minor component in zooplankton, *Gyrodinium* spp. These results have shown that prediction of the ecosystem response to anthropogenic or natural perturbation is still a challenging issue, and further studies on the ecosystem structure and the functions of its components are needed.

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Phytoplankton community response to iron and temperature gradient in the NW and NE subarctic Pacific Ocean

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During the 2001 SEEDS (**S**ubarctic Pacific Iron **E**xperiment for **E**cosystem **D**ynamics **S**tudy) and 2002 SERIES (**S**ubarctic **E**cosystem **R**esponse to **I**ron **E**nrichment **S**tudy) experiments, on-board bottle incubation experiments were carried out by adding different amounts of iron to elucidate phytoplankton community responses to iron concentrations. Temperature gradients from 5 to 18°C were also applied to the incubation experiments because temperature affects growth rate and metabolic functions, such as enzyme reactions, in phytoplankton cells. At the same iron concentration, specific chlorophyll *a* increase rates (growth rates) for micro-sized phytoplankton (>10 μm) were the highest, between 9 and 13°C, almost doubled from 5 to 9°C. The surface mixed layer temperature was 9°C at the beginning of iron fertilization, but was 5°C just two weeks before. We believe that this drastic increase in growth rate with temperature was a reason for the highest chlorophyll *a* increase in SEEDS among all the mesoscale iron enrichment experiments conducted in the HNLC regions.

SERIES: Copepod grazing on diatoms

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During the **S**ubarctic **E**cosystem **R**esponse to **I**ron **E**nrichment **S**tudy (SERIES), the phytoplankton population depleted dissolved silicate, bringing an end to a bloom which had increased diatom biomass in the patch by more than 10-fold over the 4-week study. Silicate has been implicated as an important ballasting material that adds density to sinking particles and increases carbon flux out of the upper ocean. Therefore, processes which enhance either the recycling or export of silicon (Si) are crucial in understanding carbon fluxes.

Phytoplankton biomass increases through the uptake of silicate, along with carbon and other macro (N and P) and micro (*e.g.*, Fe) nutrients. The increased biomass is either recycled in the upper ocean, or is "exported" as increased animal biomass or as sinking detritus (Fig. 1). Open ocean ecosystems export ~10% of primary production, the balance being remineralized in the surface layer. Any incorporation of organic matter into other trophic levels does not include silicon, causing its enrichment in detrital materials. Thus, particles sinking out of the subarctic surface layer are commonly enriched in Si compared with C or N.

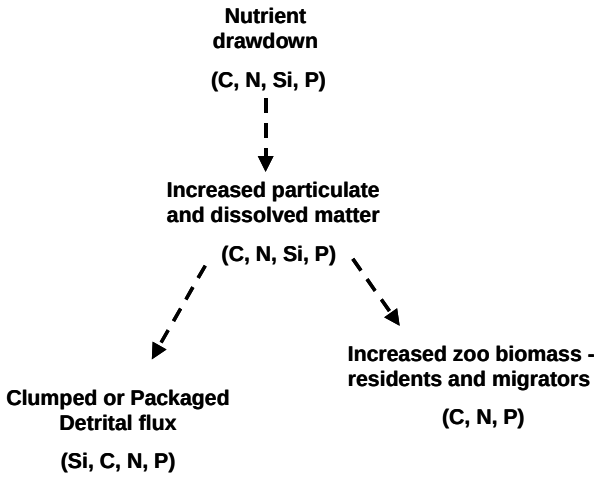

Fig. 1 Elemental cycling in the upper ocean.

At Ocean Station Papa (OSP), silicate is used by diatoms predominantly in May and June (Whitney and Freeland, 1999). This is the time of year that the major copepod species, *Neocalanus plumchrus*, is actively grazing (Mackas *et al.*, 1998). May–June is also the period that sees the highest fluxes of detrital material into the interior of the ocean at OSP (Wong *et al.*, 1999). Since the SERIES experiment was conducted in July of a warm, strongly stratified year, it is likely that *N. plumchrus* had entered diapause before iron fertilization took place. Thus a major grazer would not have been active to crop the diatom bloom that iron enrichment stimulated. To look at the effects of grazers on the diatom community in SERIES, major copepod species (the dominant macro-zooplankton) in both the water column and from sediment traps were analyzed for Si content. Ten to 20 copepods were picked from samples then dessicated and digested with 1% Na_2CO_3 solution in an 85°C bath for 2 to 4 h. Samples were then analyzed for silicate using standard Autoanalyzer procedures.

Silicon dynamics for SERIES is summarized in Figure 2. Silicate was rapidly drawn down between July 23 and 28, to the point where it was likely limiting diatom growth (along with iron). The diatom bloom resulted in an accumulation of particulate Si in the upper 20 m by July 26 and a subsequent export of this material to sediment traps at 50 m depth. The copepod community showed some response to phytoplankton growth (*e.g.*, Fig. 3), their numbers increasing during the bloom. However, an increase in numbers is likely the result of the patch collecting or attracting grazers as it drifts. Copepod reproduction is not rapid enough to account for increased numbers.

Copepods attracted into sediment traps (Fig. 4) show an increased activity in the latter part of the study. The dominant (>1 mm) zooplankton collected by traps were the copepods *Eucalanus bungii* and *Neocalanus cruistatus*. Collections of over 150 copepods per trap cylinder per day, largely

E. bungii, are much higher than actual numbers of copepods collected in net tows (tows = 3,000 m^{-2}, traps = 26,000 m^{-2}). Also, the 100- and 125-m traps, which were imbedded in the pycnocline rather than the mixed layer, collected more *E. bungii* and *N. cristatus* in the final trap deployments.

In Figure 5, we show our results for Si content in copepods collected by net tows or in sediment traps. The data set is incomplete in late experiment, but provides information on grazing by various species. The smaller copepods, *Pseudocalanus, Oithona* and *Metridia* may graze on diatoms, but because of their size contain little Si. Most interesting is the trend in *E. bungii* showing increased Si content at the time of the Si export event. These copepods appear to have increased their feeding on diatoms in the last several days of SERIES.

To consider whether a species such as *E. bungii* could have contributed to the export of Si from the surface layer during SERIES, we construct a budget based on the number of these copepods collected by net hauls and on their Si content from traps. The budget shows that 3,000 copepods containing ~5 nmol Si $copepod^{-1}$ (0.15 µg $copepod^{-1}$ in Fig. 5) yields 15 µmol m^{-2} in gut content, compared with 5 to 15 mmol m^{-2} d^{-1} Si flux to 50 m depth. Even if copepods were producing fecal pellets containing this amount of Si every 30 minutes throughout the day, they would only contribute 1 to 2% of the Si flux observed during SERIES.

These results should be considered preliminary. Further analyses of increases in copepod body size will provide independent evidence on the importance of grazers as a sink for organic material. At the present, we can only speculate that copepod grazing did not contribute significantly to export from the patch. However, a cautionary note is that patch net tows were carried out during daylight hours. Goldblatt *et al.* (1999) showed that migrating species such as *N. plumchrus* are more abundant in surface waters at night than during the day in spring.

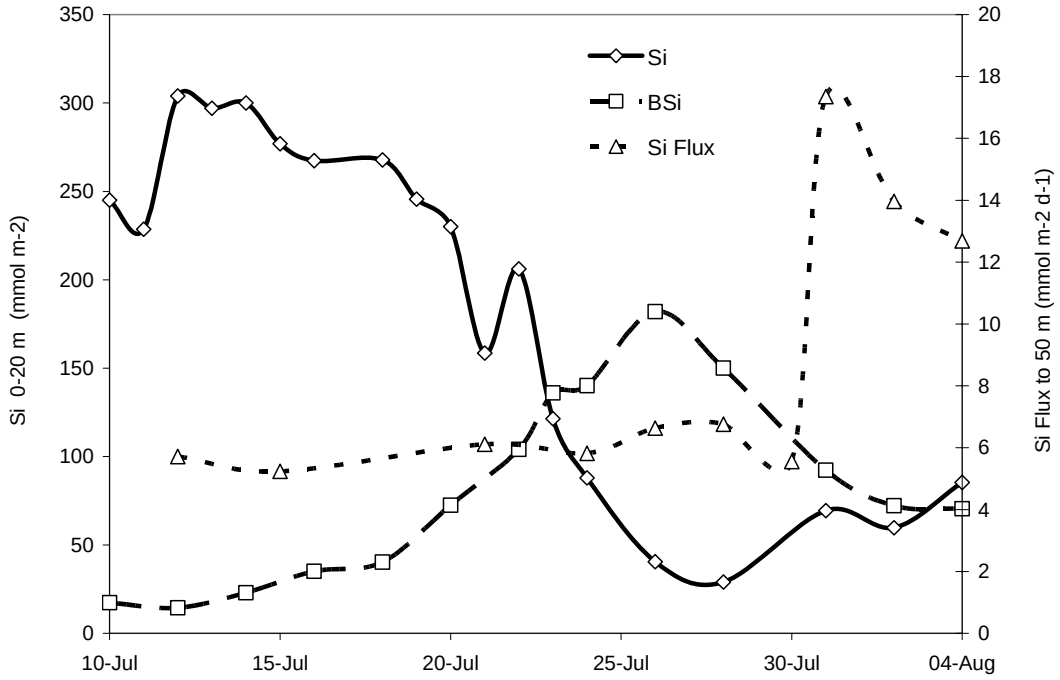

Fig. 2 Silicon dynamics in the SERIES patch and transport to a sediment trap at 50 m below the patch.

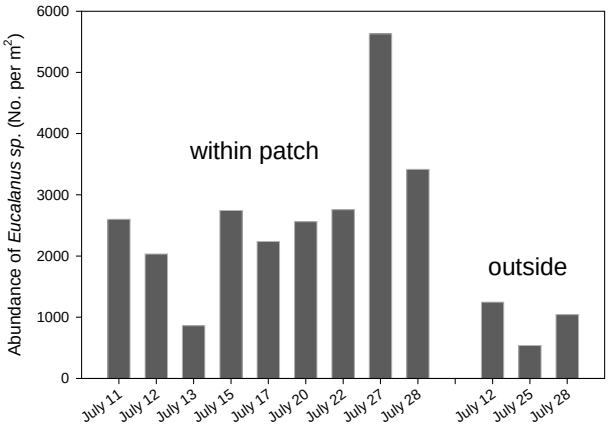

Fig. 3 Abundance of *Eucalanus bungii* inside and outside the patch from 150-m tows collected in daylight hours.

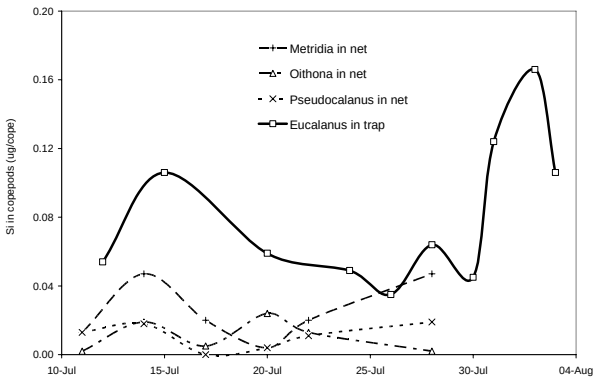

Fig. 5 Si content of copepods collected either by net haul or by removal as swimmers from sediment traps.

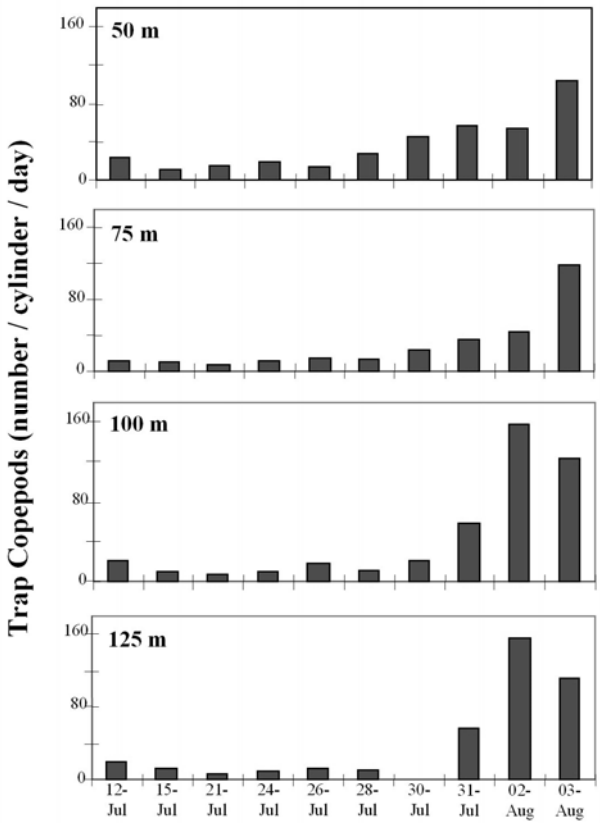

Fig. 4 Number of swimming copepods (>1 mm) removed from sediment trap materials during SERIES. The copepods *Eucalanus bungii*, followed by *Neocalanus cristatus*, were the most dominant.

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The Southern Ocean Iron Enrichment Experiment: The nitrogen uptake response

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Introduction

Over the last decade considerable effort has been directed toward understanding the relationship between phytoplankton productivity and the availability of iron, particularly as a cause for the lack of significant autotrophic growth in high nitrate, low chlorophyll (HNLC) regions of the open ocean. The results of iron-enrichment shipboard incubation (grow-out) experiments and *in situ* iron-enrichment experiments conducted in the subarctic North Pacific, equatorial Pacific, and the Southern Ocean strongly support the idea that phytoplankton growth rates and biomass accumulation in HNLC areas are limited, at least in part, by the availability of iron. Despite the abundance of nitrate in the surface waters of these regions, phytoplankton are supported primarily by regenerated N forms (*i.e.*, ammonium and urea), presumably because of the lower energetic costs needed to utilize these reduced substrates compared to nitrate when iron is limiting (*e.g.*, Raven, 1990). In this current study, the planktonic nitrogen uptake response to iron addition is described in the largest of these HNLC regions — the Southern Ocean during the Southern Ocean Iron Experiment (SOFeX) conducted in the austral summer 2002 (Coale *et al.*, 2004). This is the first report documenting the nitrogenous uptake response of natural phytoplankton communities to *in situ* iron fertilization of the Southern Ocean, although two previous open-ocean iron-enrichment experiments have been conducted in the Southern Ocean, one in the Australian sector [**S**outhern **O**cean **I**ron **RE**lease **E**xperiment (SOIREE, Boyd *et al.*, 2000)] and the other in the Atlantic sector [Eisen (iron) Experiment (EisenEx, Gervais *et al.*, 2002)]. The present study describes two nitrogen processes affected by the alleviation of iron limitation in the southern patch of SOFeX: 1) the nitrogenous nutrition (nitrate, ammonium, nitrite and urea) of the natural phytoplankton communities, and 2) the potential inhibitory effects of ammonium on the observed uptake rates of nitrate.

Materials and methods

General

The SOFeX study was conducted at two sites both north and south of the Antarctic Polar Front Zone (APFZ), in low- and high-silicate waters, respectively. We focus here on the 'southern patch' which was characterized by high nitrate (~28 μM) and silicic acid (~ 60 μM) concentrations, an average mixed layer (ML) temperature of –0.5°C and ML depth of 45 m. Iron (as acidic iron sulphate) and the inert tracer sulfur hexafluoride (SF_6) were added to a 15 by 15 km patch in the vicinity of 65°S, 172°W during four separate injections beginning on January 24, 2002 (day 0). The patch was then tracked and monitored by three research vessels in a Lagrangian fashion for one month. Details of the experimental methodology of the SOFeX, patch dilution and mixing rates, biological and chemical responses, and export flux are presented elsewhere (Bishop *et al.*, 2004; Buesseler *et al.*, 2004; Coale *et al.*, 2004).

Sampling and N-uptake experiments

Samples for nitrogen uptake experiments were collected from within and outside (control waters) of the iron-enriched patch using 30-L trace-metal free Go-Flo bottles mounted on a trace-metal clean, instrumented rosette (Hunter *et al.*, 1996); all subsequent sub-sampling and manipulations were conducted within a laminar-flow hood (HEPA) using trace-metal clean techniques (*e.g.*, Fitzwater *et al.*, 1982). Chlorophyll *a* concentration was measured by *in vitro* fluorometry (Parsons *et al.*, 1984) and nitrogen uptake rates were determined using the ^{15}N isotope technique (Dugdale and Wilkerson, 1986) and on-deck simulated *in situ* incubations of tracer-level enriched samples. The ammonium uptake rates reported have not been corrected for the effects of isotopic dilution (Glibert *et al.*, 1982), and thus should be considered as

conservative estimates. The inhibitory effects of NH_4^+ on NO_3^- uptake were determined by inoculating 1.2-L or 280-mL polycarbonate bottles with a tracer-level (< 10% of ambient NO_3^-) concentration of ^{15}N-labeled sodium nitrate (98.25 atom %; Cambridge Isotope Laboratories) and a series of 9 to 10 concentrations (conducted in duplicate) of unlabeled ammonium sulfate ranging from 0.05 to 10 µM. Samples were incubated on-deck in clear, spectrally corrected (blue) Plexiglas® deck incubators at the ambient *in situ* temperature with photosynthetic photon flux density (PPFD) attenuated to the light depth of collection (47% of the incident surface flux). Incubations were terminated by filtration (< 80 mm Hg) after 8.5–9 h onto precombusted Whatman® GF/F filters (2.5 cm; 4 h at 450°C), and frozen in polypropylene cryovials until mass spectrometric analysis ashore.

Inhibition parameters

The inhibition of NO_3^- uptake by NH_4^+ was determined by fitting the absolute NO_3^- uptake rate versus NH_4^+ concentration data to two different functions: a simple 3-parameter exponential model (Varela and Harrison, 1999) and a modification of the inverse Michaelis-Menten equation (Harrison *et al*., 1996). The curve fitting was completed using a computerized, iterative non-linear least-squares technique (Kaleidograph®; Abelbeck Software) which utilizes the Levenberg-Marquardt algorithm (Press *et al.*, 1992). Details and the actual equations employed are presented in Cochlan and Bronk (2003).

Results and discussion

The fertilization of a patch of the surface waters of the Southern Ocean with small quantities of iron resulted in a massive bloom of phytoplankton (*ca.* 20-fold increase), and a measurable draw-down of nitrate (*ca*. 2 µM; Coale *et al.*, 2004). Coincident with the increase in phytoplankton biomass were dramatic increases in nitrate utilization rates by phytoplankton in the upper mixed layer of the south patch. Absolute (transport) uptake rates increased by a factor of *ca.* 25 in the south patch relative to outside (control) regions (Fig. 1). Addition of iron also greatly increased biomass (particulate nitrogen) specific NO_3^- uptake rates by *ca.* 10-fold, indicative of faster rates of NO_3^- consumption per unit phytoplankton biomass, a result similar to those reported for iron-amended bottle experiments conducted previously in HNLC regions of the Southern Ocean (Timmermans *et al.*, 1998; Cochlan *et al.*, 2002).

The cycling of nitrogen is dramatically affected by iron availability. The extent to which iron enrichment allows for the utilization of new forms of nitrogen may reflect a source of community growth, and at steady state, the subsequent flux which is unrealized in an iron-deficient system. Throughout the 28-day monitoring period of SOFeX, the proportion of NO_3^- uptake to the total N (NO_3^-, NO_2^-, NH_4^+ and urea) uptake was measured and can be used to estimate 'new' production – the amount of total production that can be exported from the system, without depleting the system (Dugdale and Goering, 1967). This uptake ratio, termed the f-ratio (Eppley and Peterson, 1979), increased from 0.1–0.2 to 0.5–0.6 in the iron-enriched waters of the southern patch within 3 weeks of the initial Fe injection (Fig. 2). The increased f-ratio indicates that alleviation of iron limitation allows for greater relative utilization of the amble nitrate reserves that would otherwise be underutilized for growth in the surface waters south of the APFZ, and confirms the role of iron limitation in the creation of HNLC conditions in the open waters of the Southern Ocean.

In order to assess the potential inhibitory effects of NH_4^+ on NO_3^- uptake rates, short-term incubation experiments were conducted with increased NH_4^+ availability on surface samples collected from both the outside waters (day 13) and inside the southern patch at the beginning (day 12) and end (day 22) of the monitoring period from the 47% light penetration depth. The NO_3^- uptake versus NH_4^+ concentration data are well described by both the three-parameter exponential model (Varela and Harrison, 1999) and the modified inverse Michaelis-Menten model (Harrison *et al*., 1996). Using the exponential model, the values for ρN_{max} (theoretical maximum NO_3^- uptake rate) were estimated for 'zero' NH_4^+ concentration at each station, and the extrapolated value subsequently used in a Michaelis-Menten function. Selected kinetic parameters derived from the two models are shown graphically in Figure 3 and presented in Table 1. These measurements allow for an assessment of the relative NH_4^+ inhibition of NO_3^- uptake rates as the iron-induced phytoplankton bloom developed. The ρN_{max} values increased

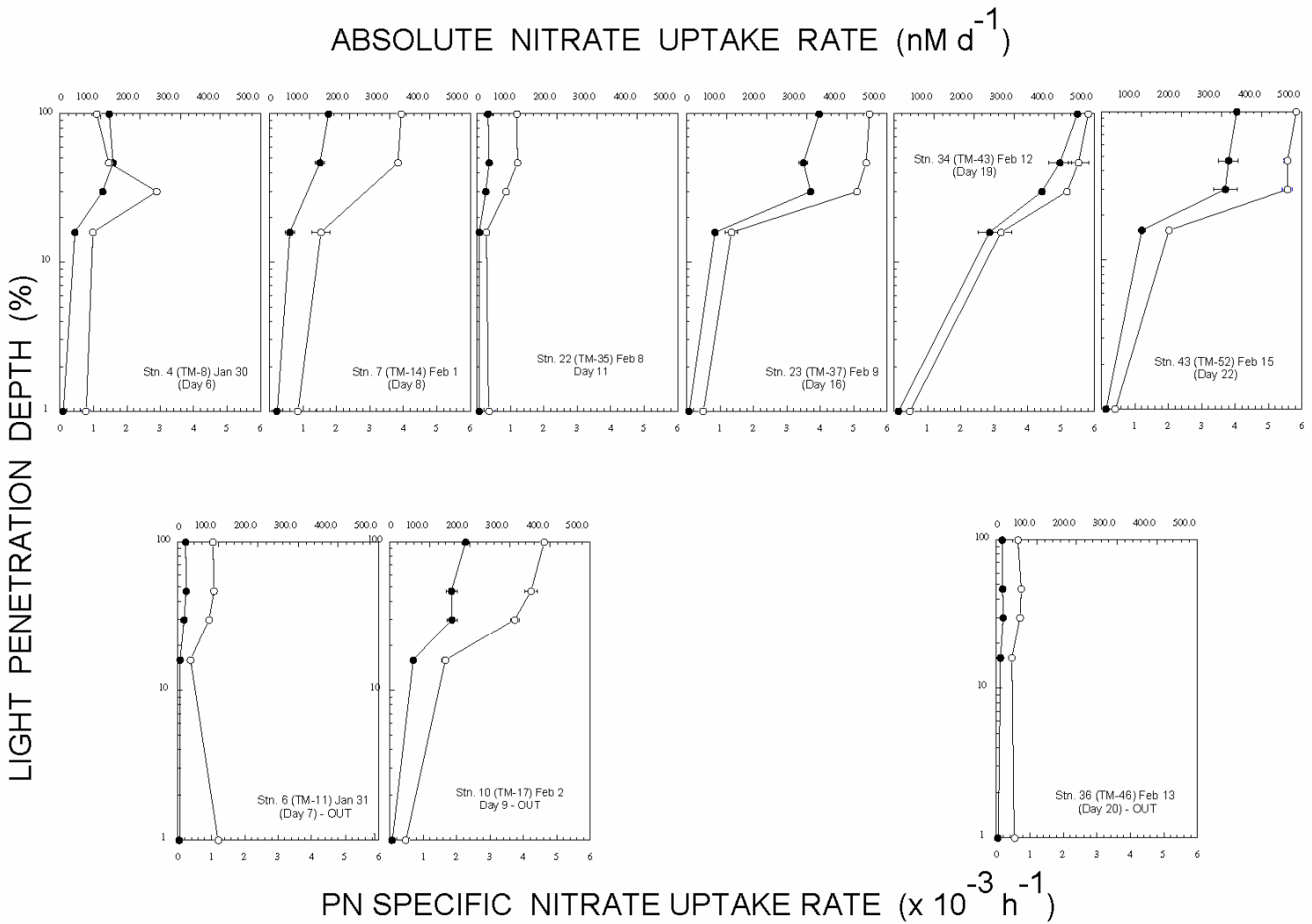

Fig. 1 Depth profiles of absolute (●) and PN-specific (○) uptake rates of nitrate in the southern iron-fertilized patch and outside (control) waters during SOFeX. Error bars represent the range of duplicate samples (n = 2); when not visible they are smaller than the symbol size.

dramatically following alleviation of iron limitation and are 4- to 8-fold greater than the ρN_{max} values determined in the outside waters. While some of the increase in this theoretical uptake rate can be ascribed to the greater biomass present following iron enrichment, the particulate nitrogen (PN)-specific uptake rates (estimated by dividing these rates by the particulate nitrogen concentrations) in the iron patch also increased and are 2- and 3-fold greater on days 12 and 22, respectively, than the outside rate. The maximal realized inhibition (I_{max}) value was greatest for the outside (control) waters (84%) and decreased to 57 and 75% on days 12 and 22, respectively. In other words, the maximum possible reduction in NO_3^- uptake rates due to NH_4^+ was lessened due to alleviation of iron limitation. The half-saturation constants of inhibition (K_I) were very low in the un-enriched waters (0.26 µM), but increased with time in the iron patch (1.09 and 1.45 µM) suggesting that greater concentrations of NH_4^+ are necessary to reduce the NO_3^- uptake rate by 50% following iron enrichment. Using these derived inhibition parameters and the ambient NH_4^+ concentrations for the outside waters (0.18 µM),

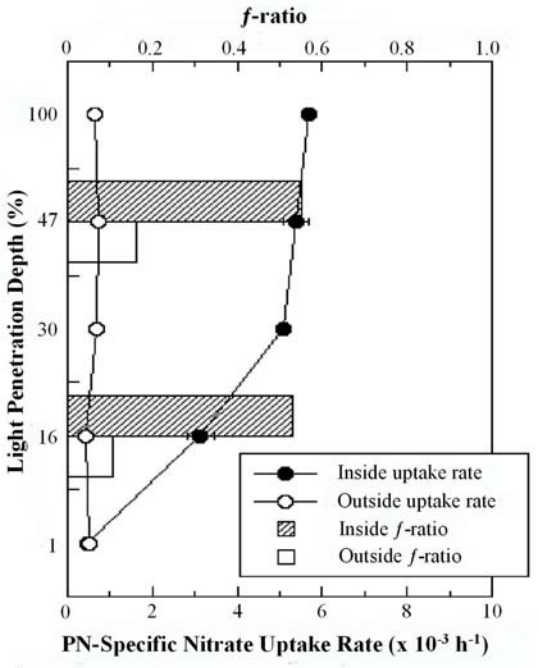

Fig. 2 Depth profiles of PN-specific nitrate uptake rates for samples collected within (iron-enriched) and outside (control waters) of the iron-enriched patch south of the APFZ. The *f*-ratios were determined at the 47 and 16% light depths, and are not corrected for the effects of isotopic dilution. Error bars represent the range of duplicate samples (n = 2).

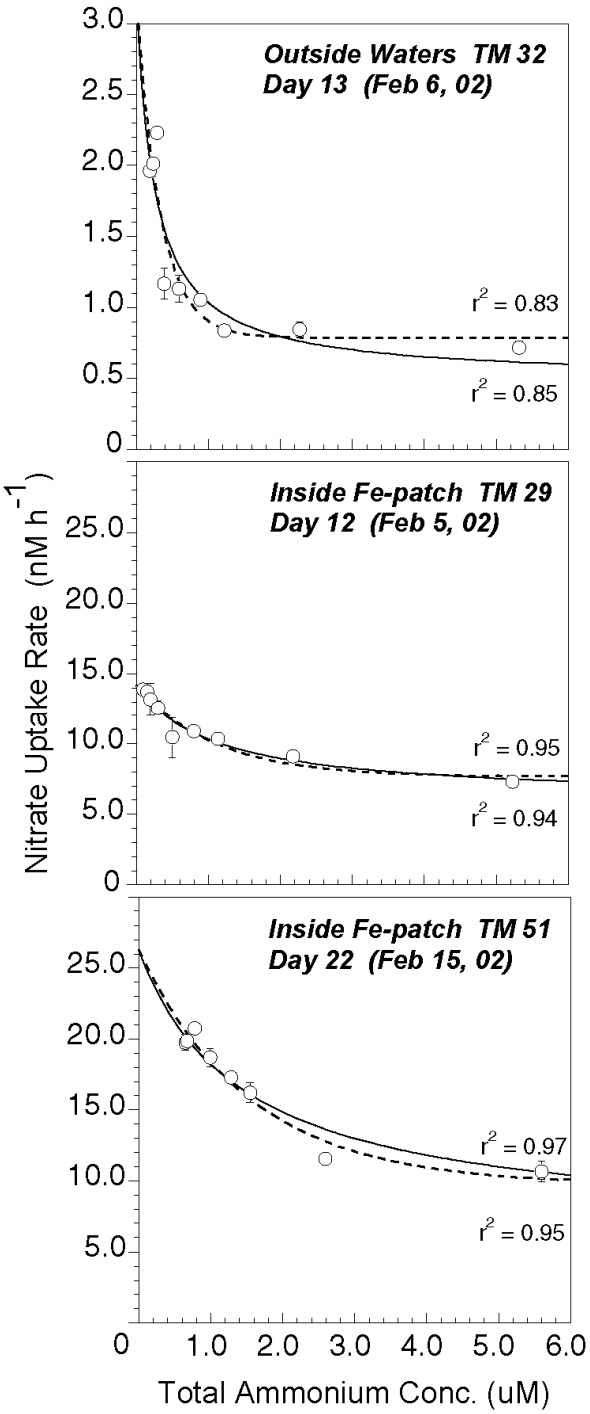

Fig. 3 Absolute NO_3^- uptake rates (nM h^{-1}) by natural assemblages of phytoplankton as a function of total (added + ambient) NH_4^+ concentration. Rates estimates are fitted directly to the 3-parameter exponential and the inverse Michaelis-Menten functions, and denoted as dashed (---) and solid (—) lines, respectively.

Table 1 Summary of the kinetic parameters describing the inhibitory effects of NH_4^+ on NO_3^- uptake by Southern Ocean phytoplankton during SOFeX.

Station Name, Cast and Day	I_{max}	Ambient NH_4^+ conc. (µM)	K_I	N_{inhib}
Outside, TM 32	0.84	0.18	0.26	2.3
Day 13	(0.067)		(0.07)	(0.67)
Fe-Patch, TM 29	0.57	0.09	1.09	9.8
Day 12	(0.061)		(0.29)	(2.6)
Fe-patch, TM 51	0.75	0.57	1.45	13.1
Day 22	(0.045)		(0.23)	(2.1)

The potential maximal inhibition (I_{max}) estimates and half-saturation constants of inhibition (K_I) were determined from the inverse Michaelis-Menten equation. The values of N_{inhib}, the NH_4^+ concentration above which no further NO_3^- uptake occurs, were approximated as $9 \times K_I$. Standard errors (SE) values of parameters are reported in parentheses.

one can compare the relative inhibitory effects of NH_4^+ on NO_3^- uptake rates at one low ammonium concentration for all stations. Based on such an analysis, this relatively low NH_4^+ concentration would decrease ρN_{max} values for outside, and iron-patch samples from days 12 and 22, by 31, 7 and 3%, respectively. These results suggest that the potential inhibitory effects of NH_4^+ on NO_3^- utilization are diminished (or dis-inhibited) by the alleviation of iron limitation in the Southern Ocean.

Conclusions

The alleviation of iron limitation in the HNLC waters south of APFZ contributes to enhanced nitrate utilization by phytoplankton; absolute uptake rates increased *ca*. 25-fold (relative to un-enriched waters) and PN-specific rates increased by *ca.* 10-fold. This enhancement of new production by iron fertilization is reflected in an increase in f-ratio from 0.1–0.2 to 0.5–0.6 in surface phytoplankton communities. Ammonium inhibition experiments, conducted on-deck, suggest that iron-replete communities are less sensitive to the potential inhibitory effects of ammonium on nitrate utilization.

Acknowledgements

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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.

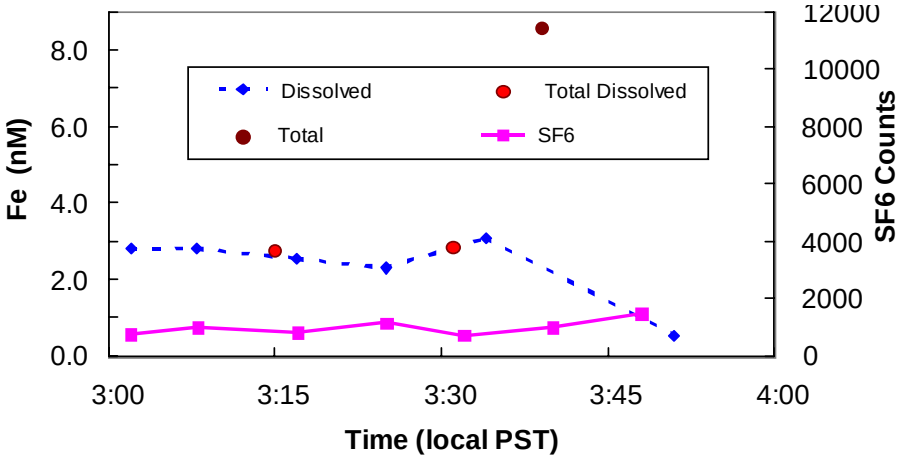

Fig. 1 Transect of iron in freshly injected patch, showing dissolved, total dissolved and total iron concentrations.

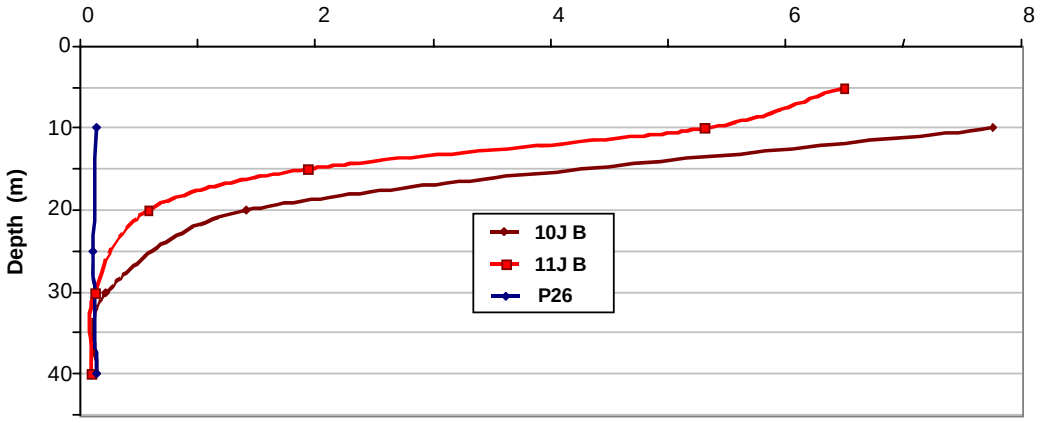

Fig. 2 Profiles of total iron for P26 prior to injection and for patch centre for the first 2 days (July 10 and 11) after injection.

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).

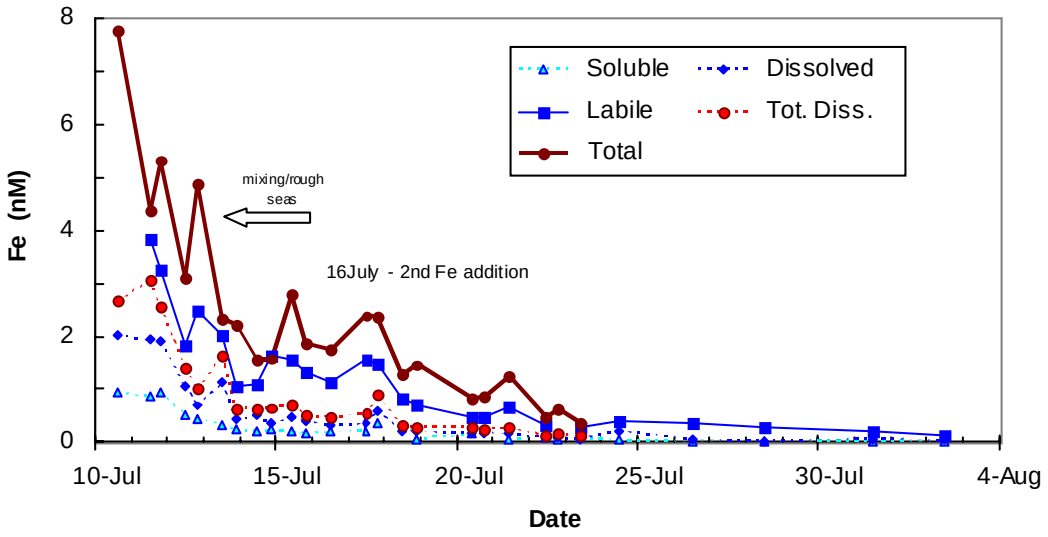

Fig. 3 Decline of 10 m surface iron over the entire experiment for all 5 measured iron phases.

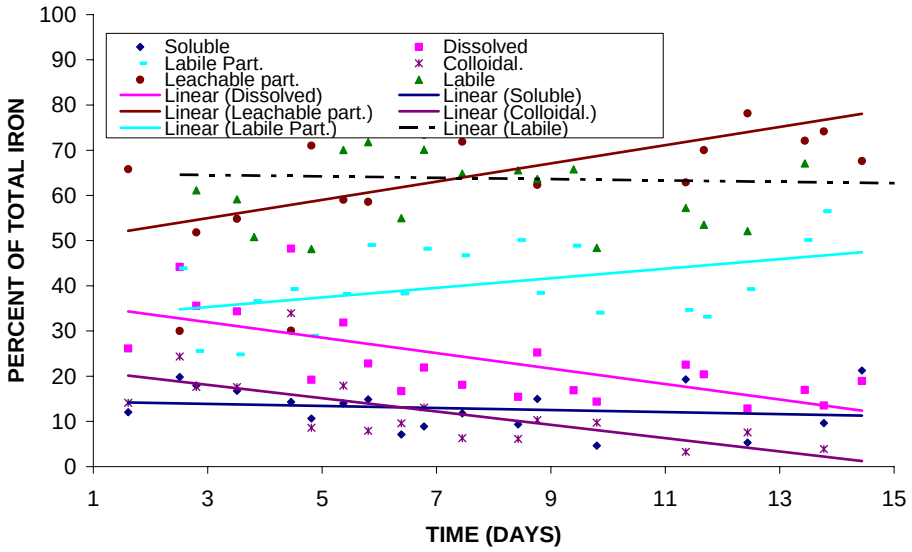

Fig. 4 Linear trends of percent of various iron phases (of total iron) over time using 10 m data

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.

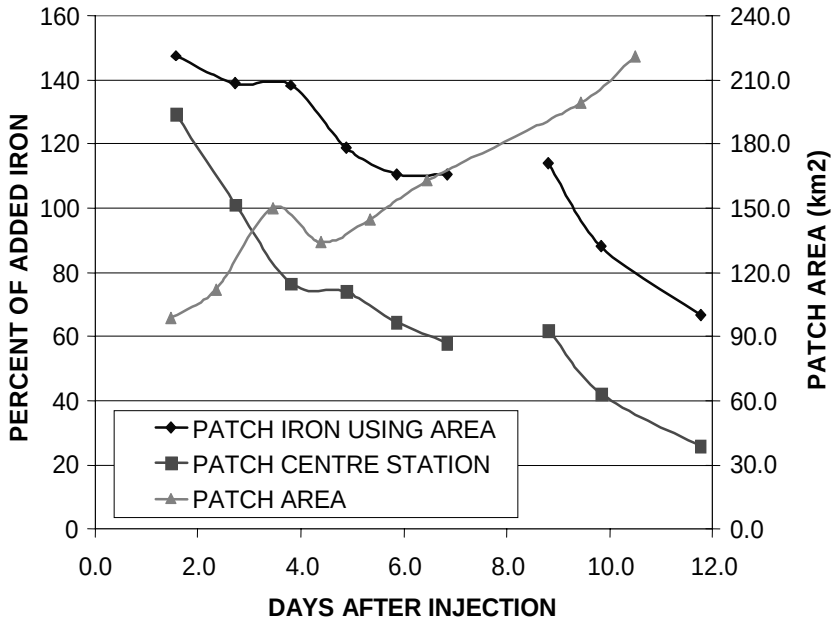

Fig. 5 Loss of integrated iron (0–40 m) as a percent of calculated iron added, with and without taking into account dilution due to patch spreading.

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

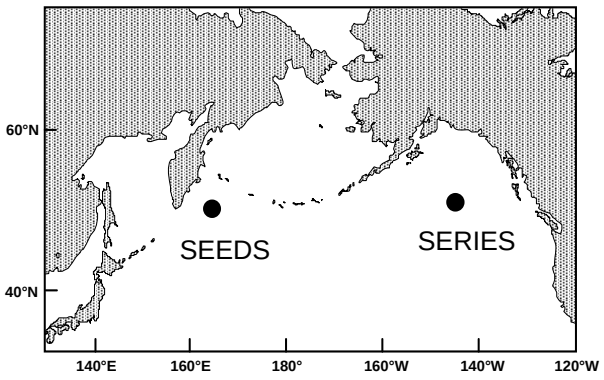

Fig. 1 Locations of *in situ* iron enrichment experiments in the western (SEEDS) and the eastern (SERIES) subarctic Pacific.

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.

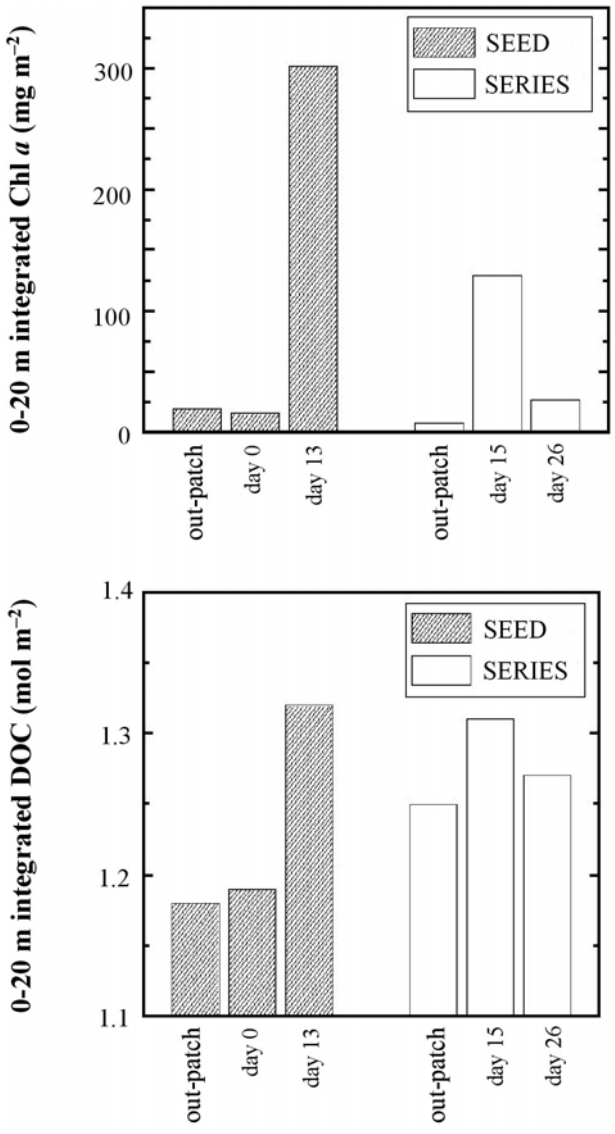

Fig. 2 Integrated values (0–20 m) for Chl-*a* (top) and DOC (bottom) during the SEEDS and SERIES experiments.

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.

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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*.

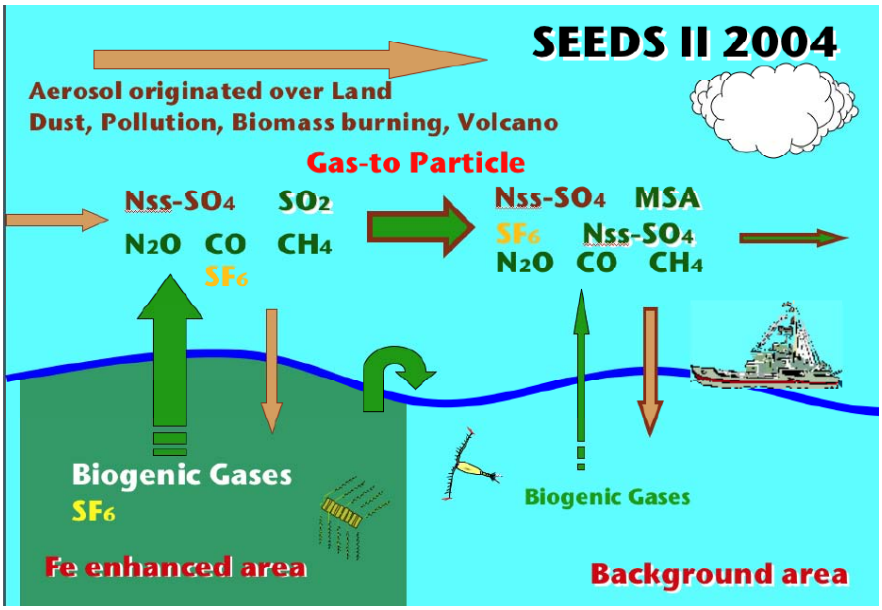

Fig. 1 Schematic image of atmospheric measurements during the SEEDS II cruise.

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.

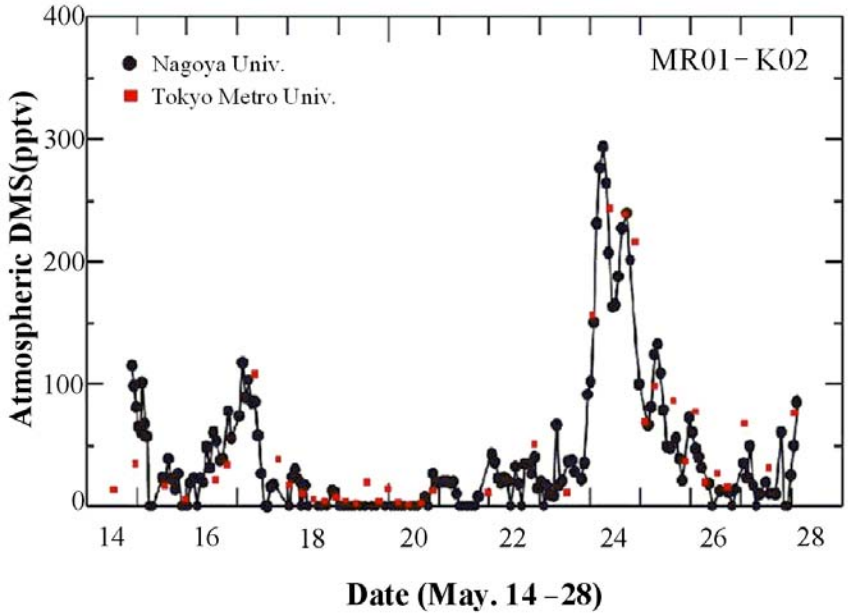

Fig. 2 Comparison of atmoshpheric DMS concentration during the R/V *Mirai* cruise. Data courtesy I. Nagao and Y. Kajii.

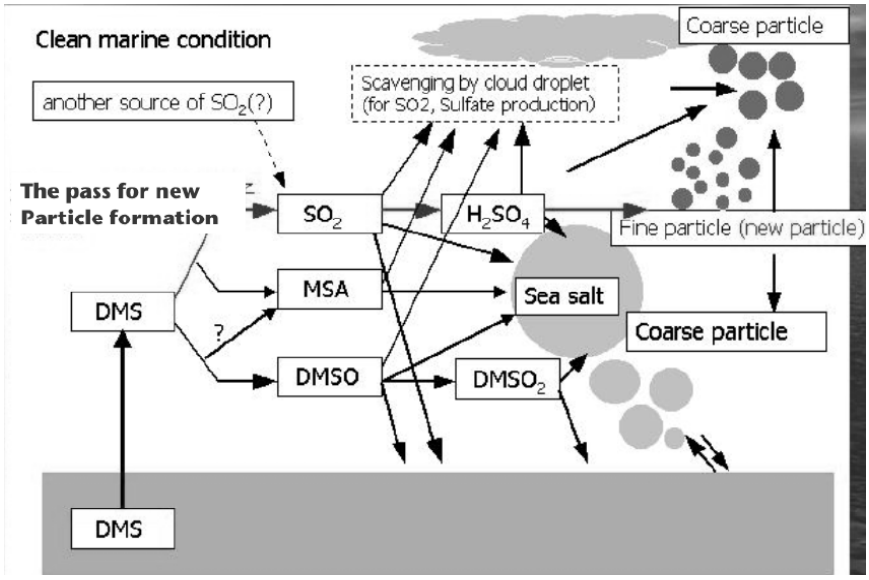

Fig. 3 Gas to particle transformation processes of DMS. Figure courtesy of I. Nagao.

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.

3.4 Prediction from Models

Modelling iron limitation in the North Pacific

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Background

The subarctic North Pacific is one of three major high nitrate, low chlorophyll (HNLC) oceanic regions, along with the Southern Ocean and the eastern equatorial Pacific. In these regions, uptake of nitrogen by phytoplankton is widely thought to be regulated by the availability of dissolved iron. The supply of dissolved iron is twofold: via atmospheric deposition of dust and via upward transport of dissolved iron from the ocean interior to the surface euphotic layer. In the subarctic North Pacific, atmospheric deposition has been considered to be the dominant source, despite little compelling evidence.

The subarctic NE Pacific Ocean, in the vicinity of Ocean Station P (OSP), contrasts with the subarctic NW Pacific, because the strong permanent halocline between 100 and 150 m depth in the NE Pacific resists winter mixing deeper than ~120 m and reduces the diffusive upward transport of dissolved nutrients from below the permanent halocline. Long-term observations at OSP, dating back to the 1950s, have given a relatively complete description of the annual cycle in physical properties, nutrients, primary production, phytoplankton chlorophyll, and mesozooplankton. Consequently, a number of modelling studies have used observations from OSP, *e.g.* Evans and Parslow (1985), Frost (1993) and Fasham (1995).

Recent Canadian models with iron limitation

As part of the Canadian JGOFS, GLOBEC and SOLAS studies, we have developed a series of increasingly complex models of the planktonic ecosystem, coupled to a 1-D mixed layer model in the subarctic NE Pacific with simplified regulation of primary production by iron (Denman and Peña, 1999, 2002; Denman, 2003; Peña, 2003; Monahan and Denman, 2004). In addition, Jeffery (2002) developed an ecosystem model for OSP with a life history representation of copepods. Our models now contain nitrate and ammonium, particulate organic matter (detritus), two size classes of phytoplankton, microzooplankton, and time-dependent grazing by mesozooplankton, specified from 20 years of net tows at OSP. A schematic of the current complexity level of our modelling is shown in Figure 1 (from Peña, 2003), along with the annual cycle for a "standard run" (Fig. 2), with parameter values selected to give results most congruent with long-term observations at OSP. We have used these models to explore ecosystem responses to changes that might accompany climate change: 2° and 5°C warming offsets, and the removal of iron limitation. Generally, these simulations result in large changes in microzooplankton biomass, small changes in phytoplankton biomass, more recycling, and in some cases, changes in export production.

Monahan and Denman (2004) used long-term observations of winds, cloudiness and radiation to develop stochastic forcing functions with statistics (mainly variance and temporal covariability) matching the observations month by month. The model was then run for 1000 years with stochastically varying forcing. With iron limitation charactistic of OSP, the modelled ecosystem annual cycle displayed considerable variability on scales out to decades, but nitrate never became limiting. Simulations of the continental margin (near Line P, Station 04) displayed nitrate limitation most years, and simulations of conditions midway along Line P (~ Station 16) displayed nitrate limitation about 30% of the summers, often for several years at a time. We have added silica into the model and plan to rerun these experiments to see if occasional silica limitation can be simulated at OSP as in observations.

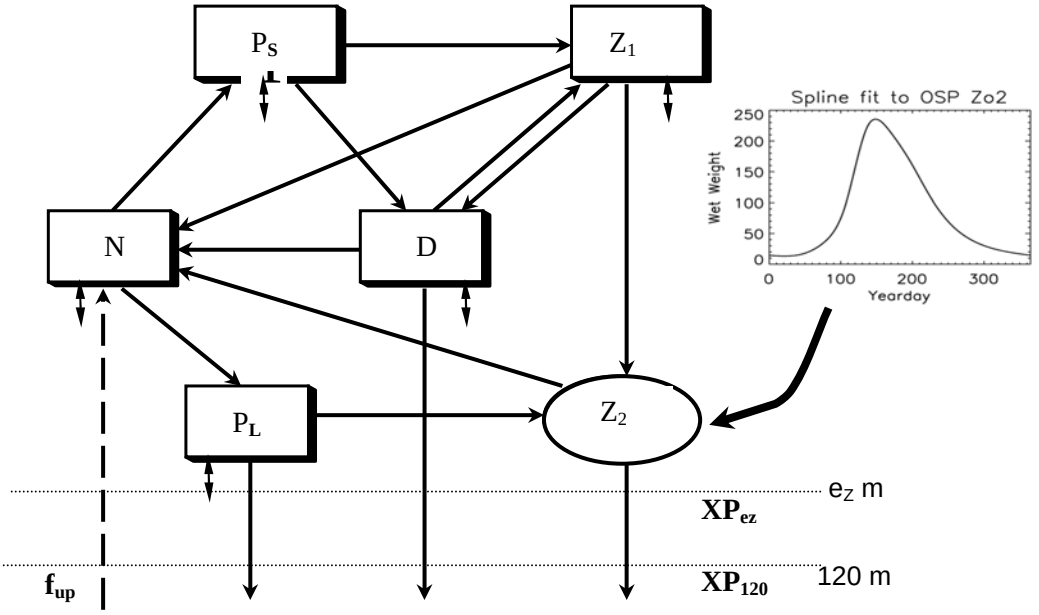

Fig. 1 Schematic diagram of the ecosystem model. Arrows indicate flows of matter through the system, doubled-ended arrows represent mixing fluxes across the base of the euphotic zone and open-ended arrows indicate the input to, and losses from, the system. The export of sinking particles across the base of th e euphotic zone and out of the model domain is denoted by XP_{EZ} and XP_{120}. The addition of nitrate in the bottom 5 layers is denoted as $f_{up.}$

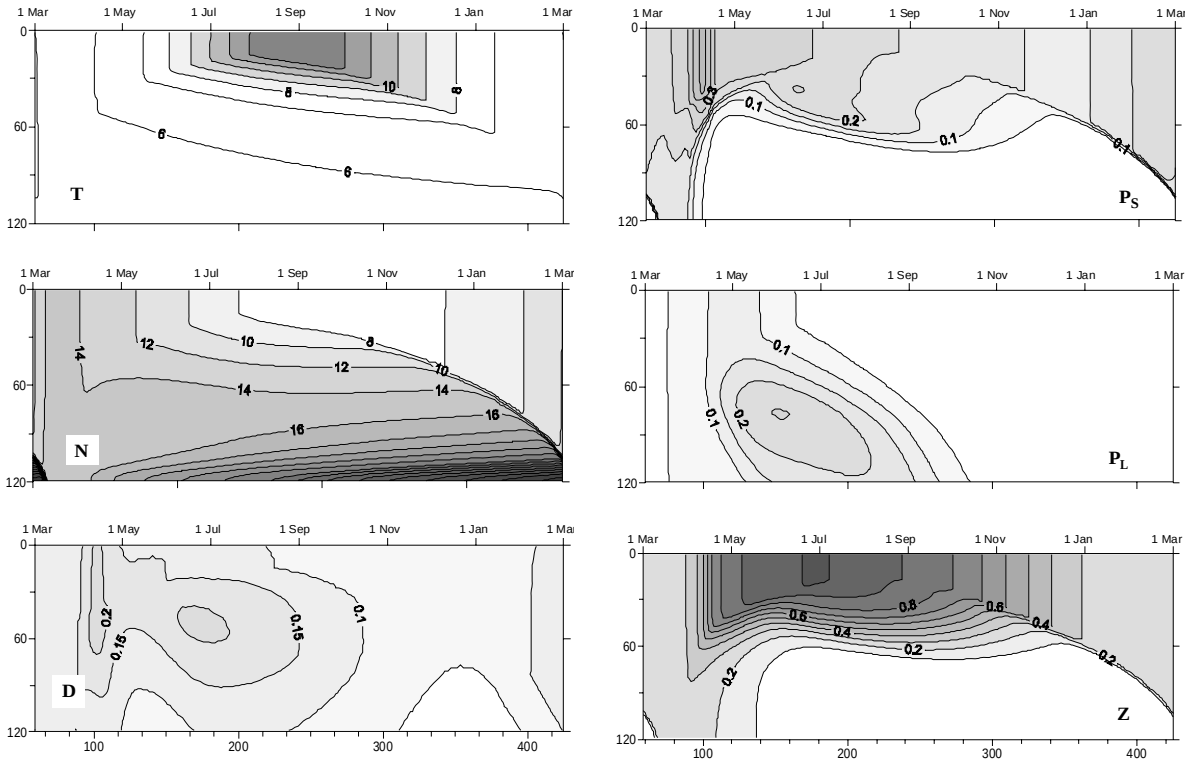

Fig. 2 Time-depth plots for the "standard" run: (left column) temperature (°C), nitrate and detritus (in mmol N m^{-3}) and (right column) small phytoplankton, large phytoplankton, and microzooplankton (in mmol N m^{-3}).

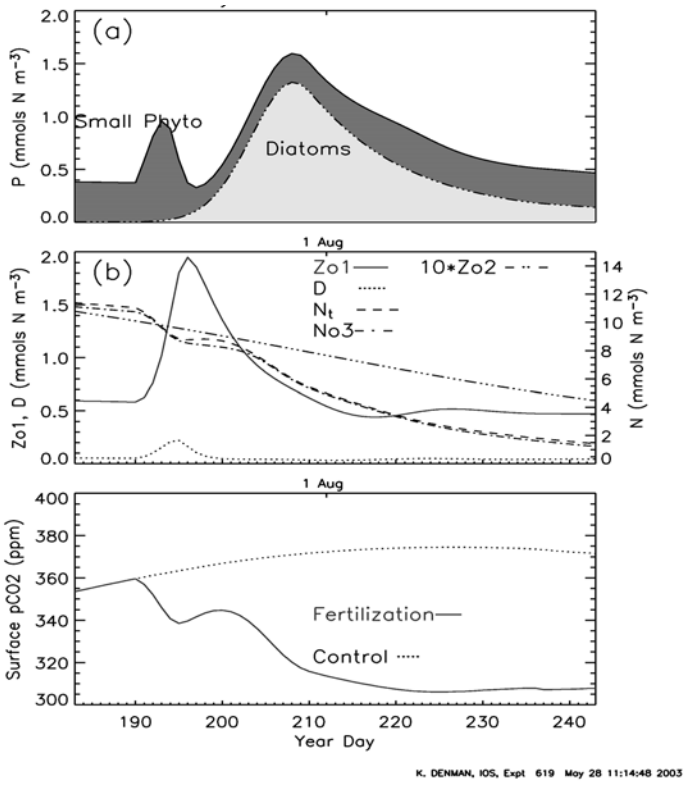

Fig. 3 Preliminary results of Monahan and Denman's ecosystem model for a 20-day fertilization.

Modelling the 2002 SERIES iron fertilization experiment

The ecosystem model described in Monahan and Denman (2004) has been applied to the **S**ubarctic **E**cosystem **R**esponse to **I**ron **E**nrichment **S**tudy (SERIES) experiment, with coupling to the inorganic carbon system and just recently to a silica cycle. Preliminary results with the fertilization, lasting 10 or 20 days, capture the main events observed during SERIES: an initial bloom of small phytoplankton followed rapidly by a bloom of microzooplankton, an eventual bloom of large phytoplankton (assumed to be diatoms), the final sinking of diatom aggregates, and the subsurface buildup of ammonium. This sequence of responses of the planktonic ecosystem is shown in Figure 3 for a 20-day fertilization, where the fraction of small phytoplankton assumed to be calcifiers was set to 0.25. The eventual drawdown of CO_2 depends on the length of the bloom and on the fraction of calcifiers. In addition, whether silica becomes limiting towards the end of the bloom depends on the assumed uptake ratio of Si:N.

Future directions

It is clear that for detailed model studies in the subarctic Pacific, a mechanistic model for iron must be developed. For a global model of the ocean carbon cycle to be included in the next generation of the Canadian Global Climate Model, we are trying to balance a detailed representation of processes, such as iron limitation, with the requirement for a model that will represent the "biotic pumps" of carbon over the whole global ocean.

Acknowledgements

We have benefitted from discussions and the work of our coauthors: Jim Christian, Debby Ianson, Nicole Jeffrey, Adam Monahan, and Kos Zahariev.

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A proposed model of the SERIES iron fertilization patch

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Introduction

Artificial iron fertilization experiments have shown that the micronutrient, iron, limits phytoplankton growth in high nutrient, low chlorophyll (HNLC) regions of the ocean (Martin and Fitzwater, 1988). It is assumed that episodic aeolian iron input to HNLC regions causes phytoplankton blooms that afterwards decline quickly. It is difficult to predict when such events will occur, so they have rarely been observed (mainly in sediment trap data).

Iron fertilization experiments allow the response of the natural system to iron addition to be studied. Besides confirming the hypothesis of iron limitation in HNLC regions, they have shown that iron often has a short residence time in the surface layer due to particle scavenging and biological uptake. In recent years the complex chemical cycling of iron in the ocean has been recognized as an additional controlling factor (Wells, 2003). However, this cycling remains poorly understood.

The species composition of phytoplankton in nutrient (including iron) replete conditions shifts to a diatom-based population. Diatoms require silicic acid, so their dominance will alter the macronutrient balance. Remineralization (dissolution) length scales of silicic acid are thought to be longer than those of nitrogen and phosphorus. Thus iron fertilization causes changes in biological community structure and the chemistry of the water column. Here, we propose a model, constrained by the subarctic ecosystem response to iron enrichment (**S**ubarctic **E**cosystem **R**esponse to **I**ron **E**nrichment **S**tudy – SERIES) data, to investigate the biogeochemical pathways of iron, nitrogen, silicic acid and carbon in the euphotic zone after a large and sudden introduction of dissolved iron.

Experiment

The SERIES experiment and results are described in detail in other papers in this report. Briefly, three ships occupied the fertilized patch over a 25-day period. The patch was tracked using the tracer, sulphur hexafluoride (SF_6). Diatom growth was exponential until iron became limiting. However, the diatom seed population was small so that initially the non-diatom species present prior to iron addition showed the largest response. The latter phase of the bloom was dominated by oceanic diatoms. Silicic acid became limiting to diatom growth before nitrogen and observations suggest that silica dissolution may be occurring at shallower depths relative to nitrogen than previously thought.

Station P (50°N, 145°W) is argued to be an excellent site for such experiments, having relatively homogeneous water properties in the horizontal. During the experiment, however, the patch sat on a strong east–west frontal gradient so that outer waters were not uniform in nutrient or salinity concentrations. In addition, the patch appears to have slipped over a distinctly different water mass in the later course of the experiment. These physical changes make it more difficult to estimate dilution or entrainment fluxes from the patch in both the vertical and the horizontal. We have designed our model to address this difficulty.

Model

The model consists of three components: physical, ecological and the iron component. Below, we discuss the physical and iron aspects of the model. We will use the ecological model of Denman (2003; also Denman and Peña, this report). Iron, carbon, nitrogen and silicic acid will be tracked as model currencies. In addition, salinity and SF_6 will be tracked to constrain the physical parameters.

Physical

We model three physical regions separated by transition zones having linear gradients in model properties. Each region is assumed to be homogeneous in properties. The main region, the inside of the patch (region 1), is described by its area, perimeter and depth, all of which are prescribed to vary in time according to the observations (Fig. 1). The depth is the mixed layer depth (MLD) (Steiner *et al.*, in press). The horizontal parameters are based on the SF_6 data (Law *et al*., in press). The area and movement of the MLD determine vertical entrainment and mixing. The MLD and the change in the perimeter determine the horizontal exchange. The remaining regions are the surrounding surface waters (region 2) and the lower layer (region 3) (Fig. 1b). Concentrations of model quantities in regions 2 and 3 will be prescribed, varying in time, based on observations.

Iron

Iron in seawater exists in a variety of chemical and physical forms, including dissolved organic complexes, colloidal and particle-bound forms. This speciation influences the residence time of iron within the mixed layer, as some forms are more readily lost from the euphotic zone by adsorbing onto sinking particles than others (Bowie *et al.*, 2001; Wu and Boyle, 2002). Because some iron species are more easily taken up by phytoplankton than others (*e.g.*, Hutchins *et al.*, 1999), speciation might also influence the bioavailability of iron.

Iron speciation for SERIES is reported in terms of operationally defined categories by filtration procedures. To make the model as consistent as possible with the observations, the model differentiates between truly dissolved, colloidal and particulate iron. The dissolved pool is further split into inorganic ferric iron Fe(III)', which includes all hydrolized species of $Fe(OH)_n^{3-n}$, dissolved inorganic ferrous iron Fe(II)', and organically complexed iron FeL.

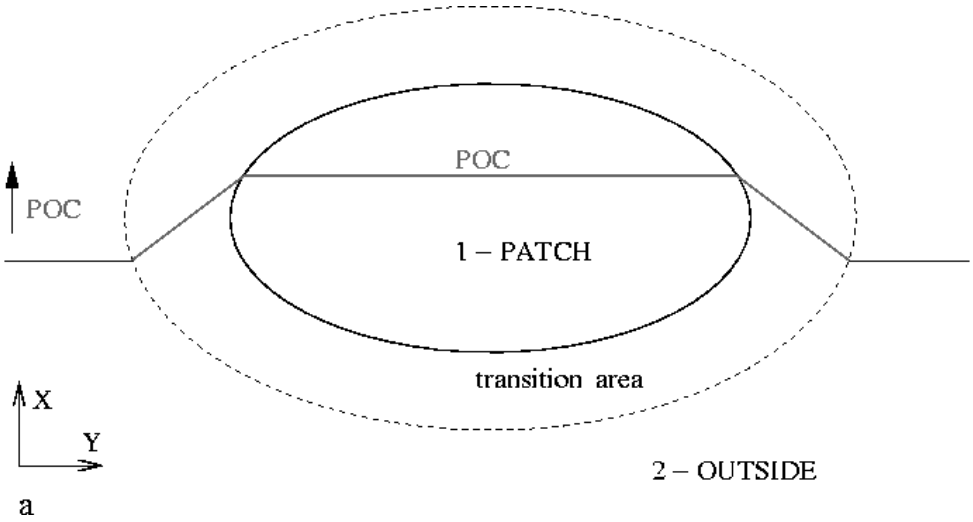

Fig. 1 The physical model structure in the horizontal showing the state variable particulate organic carbon (POC) in region 1 (the patch), region 2 (the outside) and the transition area between (a) and the vertical showing salinity (S) in the upper (region 1, the patch) and lower (region 3) layer with the transition between (b).

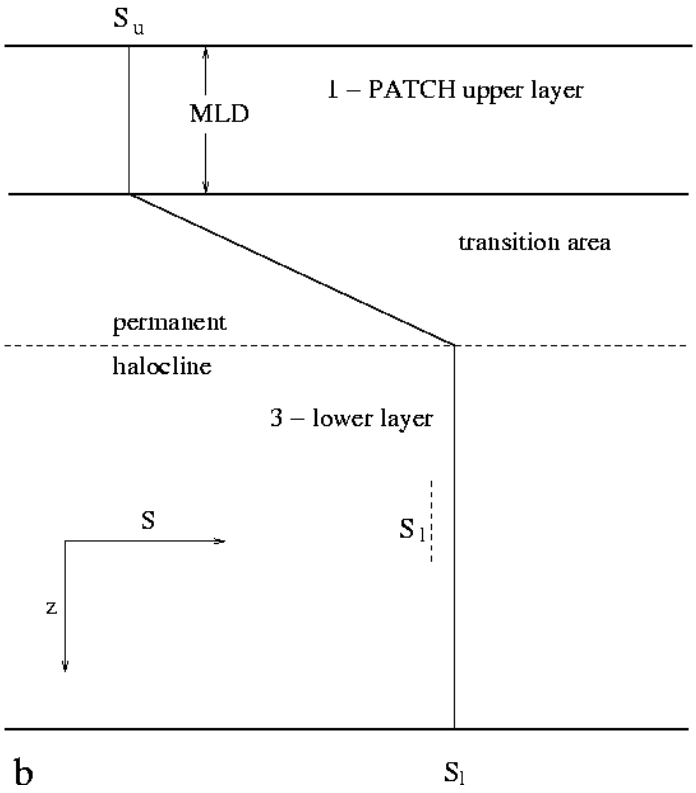

Fig. 1 Continued.

A number of processes are known to convert iron in seawater from one of these forms into another. The model includes the processes of:

- complex formation and dissociation involving organic ligands (*e.g.*, Witter *et al.*, 2000);
- photoreduction of the different iron forms, both directly (*e.g.*, Barbeau *et al.*, 2003) and indirectly by photoproduced superoxide (Voelker and Sedlak, 1995);
- oxidation of Fe(II)' by oxygen, superoxide and hydrogen peroxide (*e.g.*, Millero and Sotolongo, 1989);
- scavenging onto particles (Nyffeler *et al.*, 1984);
- colloid formation (Johnson *et al.*, 1994);
- colloid aggregation (Wen *et al.*, 1997).

We assume that the fast reactions transforming iron between the three dissolved forms are in instantaneous equilibrium, such that the speciation of dissolved iron can be calculated diagnostically (Fig. 2).

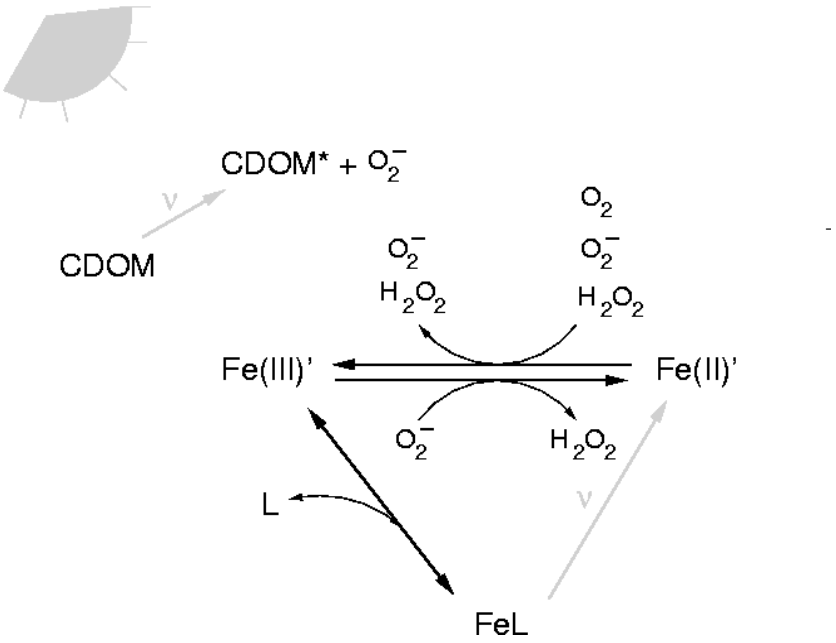

Fig. 2 The diagnostic portion of the iron model showing the species of dissolved iron and their transformations. Photoproduction of O_2^- from coloured dissolved organic matter (CDOM) causes reduction of Fe(III)'.

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APPENDIX 1

Report of the 2000 Planning Workshop on Designing the Iron Fertilization Experiment in the Subarctic Pacific

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A1.1 2000 WORKSHOP SUMMARY

The workshop on "Designing the Iron Fertilization Experiment in the Subarctic Pacific" was held October 19–20, 2000 in Tsukuba, Japan. The workshop was co-sponsored by PICES and CRIEPI (Central Research Institute of Electric Power Industry, Japan).

The specific objectives of the workshop were to:

1. Establish the current knowledge about the role of iron in limiting phytoplankton production in the subarctic Pacific;
2. Identify the specific questions that should be answered by the *in situ* iron fertilization experiment in the subarctic Pacific;
3. Initiate planning for the experiment, including logistics and funding, *etc*.

The workshop had the following scientific sessions:

1. General overview of IronEx and SOIREE, iron chemistry and biology in seawater;
2. Chemisty in the North Pacific and IronEx;
3. Biology in the North Pacific and IronEx;
4. Physics in the North Pacific and iron addition techniques.

The workshop was very successful thanks to 19 excellent presentations and the spirited discussion from the 39 participants.

A1.1.1 Proposed experiment summary

Background

The North Pacific is one of the three large high nitrate, low chlorophyll (HNLC) regions, along with the equatorial Pacific and the Southern Ocean that has been identified to be iron-limited (Martin *et al.*, 1991). Large-scale iron enrichment experiments have been conducted in the equatorial Pacific (IronEx II; Coale *et al.*, 1996) and in the Southern Ocean (SOIREE; Boyd *et al.*, 2000).

There are two prominent gyres in the North Pacific, the Alaska Gyre (hereafter called the Eastern Subarctic Gyre (ESG) with Station P on its southern edge) and the Western Subarctic Gyre (WSG). The input of iron for the North Pacific is thought to come mainly from the atmospheric deposition of Asian dust from the Gobi Desert (Duce and Tindale, 1991). Hence, there is a strong zonal gradient in iron deposition with the WSG receiving more dust than the eastern gyre. Evidence for this gradient in atmospheric iron deposition can be seen in the concentration gradient of soluble iron (0.85 nM in the WSG versus 0.53 nM in the ESG), and in the phytoplankton community (the WSG has more centric diatoms and a spring bloom, while the ESG has smaller cells (prymnesiophytes and prasinophytes) and more pennate diatoms and no spring bloom (Kudo, pers. comm.)). Opal dominates the carbon flux in the WSG while $CaCO_3$ dominates the flux in the ESG (Kudo, pers. comm.). The WSG has been studied mainly by Japanese scientists, while one site in the ESG (Station P) has been studied mainly by Canadian scientists (*e.g.*, see *Deep-Sea Research II,* Vol. **46** on Canadian JGOFS). An extensive comparison of the different trophic levels in the WSG and the ESG has recently been summarized in a special volume of *Progress in Oceanography* (Vol. **43** (2/3) and in particular, see Harrison *et al.*, 1999; Banse and English, 1999) and hence, a thorough background of information exists for designing our proposed iron enrichment experiments. We are proposing to continue this previously successful collaboration between Japan and Canada and invite international collaborators to join us in these intensive large-scale iron enrichment experiments where we have gaps in our expertise.

There are several strong reasons to conduct two large-scale iron enrichment experiments along this large-scale iron deposition gradient in the WSG (with high deposition) and in the ESG (with low deposition). These two sites are located in a quiescent area of the ocean with a shallow mixed layer depth in summer (20–30 m), a strong relatively shallow pycnocline (~100 m), weak and well defined surface currents, few frontal areas, and an excellent long-term time series (spanning more than 40 years in the case of Station P in the ESG).

Furthermore, each site can be reached in 2 to 3 days' travel time from major oceanographic laboratories in Japan and Canada. Therefore, this proximity will facilitate a revisit to the sites to determine the fate of the bloom and the associated response of grazers, climate change biogas production, and ligand production by the microbial community.

Shipboard iron enrichment experiments have revealed that centric diatoms grow in WSG water (Kudo, pers. comm.), in contrast to a pennate diatom-dominated community in the ESG (Martin *et al.*, 1991). This difference in the final phytoplankton community will allow comparisons in the response of grazers, carbon flux, the production of climate change biogasses and a wide range of other parameters.

The iron enrichment experiment in the WSG in particular, will represent a simulation of the annual episodic dust input from the Asian continent. Future plans of the Japanese **S**urface **O**cean **L**ow **A**tmosphere **S**tudy (SOLAS) program are to determine the input and effects of one of these dust events on the WSG. Therefore, it is important that a simulated, controlled addition of iron proceed after assessing the response of the WSG to a natural episodic dust event.

The iron enrichment experiment in the WSG and ESG will be conducted with the same methods and key principal investigators (Kenneth H. Coale, Phillip W. Boyd, and Cliff S. Law) as used in IronEx II and the **S**outhern **O**cean **I**ron **RE**lease **E**xperiment (SOIREE). Therefore, these two iron enrichment experiments and IronEx and SOIREE will offer an important contrast along a latitudinal gradient. The subarctic North Pacific represents a site where biological and chemical reactions (based on surface water temperature) should be intermediate between the previous tropical and polar iron enrichment sites. For example, the bloom developed very quickly in IronEx II (Coale *et al.*, 1996) while in SOIREE, the bloom appeared to last >40 days according to SeaWiFS images (Boyd *et al.*, 2000).

Hypotheses

The North Pacific has two prominent gyres, the western and eastern subarctic gyres (WSG and ESG). These two gyres are characterized by relatively uniform distributions in temperature, salinity, macronutrients, and light, yet they have strong zonal gradients in atmospheric iron deposition between the WSG and the ESG.

We hypothesize that:

1. the difference in episodic iron deposition gives rise to distinct phytoplankton communities (*e.g.*, centric diatoms in the WSG versus pennates in the ESG) which characterize these biogeochemical provinces;
2. the biogeochemical response of any given province (air–sea fluxes in biogases, export flux of carbon, *etc.*) is driven by episodic events such as atmospheric iron deposition.

To test these hypotheses, an iron enrichment experiment, on the scale of the entire community, is required in each gyre such that the biological community response and the resultant geochemical signals can be measured. These iron enrichment experiments will simulate natural episodic dust deposition events that occur annually, especially in the WSG.

In addition to measuring the response of a wide range of biogeochemical parameters to a large-scale iron enrichment, we hypothesize that:

- the WSG will have a higher carbon flux dominated by an opal flux, in contrast to the ESG which will have a lower carbon flux dominated by a $CaCO_3$ flux. Thus the efficiency of the biological pump will be higher in the WSG than in the ESG;
- there will be a larger response (more grazing) by the mesozooplankton in the WSG than in the ESG, which could lead to an increase in carbon flux through fecal pellet production;
- there will be more biogas production, especially dimethyl sulphide (DMS) production, due to the larger number of prymnesiophytes in the ESG compared to the WSG;
- there will be more ligands produced by the microbial community in the ESG than in the WSG because the microbial loop is more dominant in the ESG than in the WSG.

Scientific questions

- What is the fate/longevity of the bloom with an emphasis on ligand production and the response of the grazers (micro and mesozooplankton)?

- What is the magnitude and characteristics of particles (carbon flux) sinking at the end of the bloom?
- What is the production of various climate change biogases (DMS, N_2O, methane, *etc.*) during and after the bloom?

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Summary of the Canadian program

We are proposing to fertilize a 64-km^2 patch of ocean near Station P in the subarctic NE Pacific during July–August 2002. Iron will be added three or four times during the 3-week experiment and a wide variety of physical, chemical and biological parameters will be measured. In particular, we will carefully document the expected increase in phytoplankton biomass and the subsequent carbon flux out of the photic zone, the drawdown in CO_2, and the production of other climate change gases such as DMS.

There are several reasons why an iron enrichment experiment should be conducted at Station P in the NE subarctic Pacific. Station P, or Ocean Station Papa (50ºN and 145ºW), has a 40-year time series of physical, chemical, and biological parameters and thus has one of the longest open ocean time

series in the world. Three large intensive sampling programs have provided detailed information, especially on biological rate process studies (SUPER, WOCE, and Canadian JGOFS). This large published data set/time series will provide an excellent background to assess the annual and interannual natural variability for evaluating the magnitude of the response to the iron addition experiment. The subarctic North Pacific represents a latitudinal gradient between the polar (Southern Ocean) and equatorial regions and therefore, an iron addition experiment at Station P will allow a comparison among the three large HNLC regions and between the eastern and western gyres in the subarctic Pacific.

The subarctic NE Pacific has physical, chemical and biological properties different from the other two HNLC regions (Southern Ocean and equatorial Pacific). In particular, it has a very shallow summer mixed layer depth, a strong, shallow pycnocline and low currents which should help to keep the iron patch intact and ensure the success of the experiment. The biodiversity of the plankton is also different from the equatorial Pacific and Southern Ocean and therefore, the response to the iron addition and the flux of carbon out of the photic zone may be different.

Unlike the equatorial Pacific, Station P is in close proximity (3 days steaming) to major research laboratories at the Institute of Ocean Sciences and the University of British Columbia and therefore, it should be easier to document the longer-term recovery from the iron addition. If the detailed documentation of the ecosystem response to a single iron addition is successful, it will allow us to proceed to the next phase — repeated iron additions and longer-term monitoring that this will require.

Key questions that have not been entirely resolved by previous iron enrichment experiments are:

- How does the change in biodiversity and foodweb structure differ for markedly different ecosystems which have been perturbed by an iron additon?
- What is the drawdown of CO_2 and, especially, the flux of carbon to the deep ocean?
- How does the production of ligands influence the iron chemistry and the longevity of the phytoplankton bloom?
- How does zooplankton grazing influence the formation of the bloom and the carbon flux (*e.g.*, fecal pellet production)?
- What is the long-term response and recovery of the ecosystem following an iron addition?
- What is the magnitude of production of other climate change gases, such as DMS, during the bloom and how is the production influenced by phytoplankton species, microbial processes and grazing?

Objectives will be to:

- measure the response of bacteria, phytoplankton and zooplankton in terms of species, standing stocks and rate processes to the iron addition;
- measure the drawdown of CO_2 and the flux of carbon to depth;
- study the relationship between ligand production and the associated changes in iron chemistry and their influence on the longevity of the phytoplankton bloom;
- assess the influence of zooplankton grazing on phytoplankton bloom formation and carbon flux;
- follow the long-term response and recovery of the phytoplankton bloom;
- quantify the production of various climate change gases during the iron enrichment experiment and assess the factors which influence the production of these biogases.

Biological oceanographic sampling

The upper 150 m will be sampled vertically (6–8 depths) each day using 12 acid-cleaned PVC samplers on a CTD/water sampler rosette system at the patch centre (determined by SF_6 levels) and in the surrounding waters. Real-time vertical profiling of temperature, salinity, transmissivity, chlorophyll *a* fluorescence and underwater irradiance (PAR, 400–700 nm) will be carried out. Discrete water samples will be analysed for: chlorophyll *a* (size-fractionated, >20, 5–20, 2–5 and 0.2–2 µm), heterotrophic bacterial abundance, microzooplankton abundance, and phytoplankton abundance (flow cytometry, epifluorescence and light microscopy). Additional samples will be incubated on deck to measure rates of primary production (^{14}C, 24 h incubation, simulated *in situ* and size-fractionated as for chlorophyll *a*, bacterial production, and microzooplankton grazing. Mesozooplankton abundance will be assessed from

150–0 m vertical hauls. The Th:U activity ratio of particles in the upper water column will be collected using a submersible pumping system.

Geochemical measurements

Two types of sampling will be done: hydrocasts and underway sampling from the vessel's non-toxic seawater supply (intake 5-m subsurface) and analysed by fluorometry (calibrated with discrete chlorophyll *a* samples every 2 days, corrected for quenching during daylight hours), and using a bubble-segmented automated nutrient analysis system, respectively. Underway samples for dissolved iron will be conducted from a clean towed batfish sampling system, and samples for pCO_2 will be drawn from the vessel's non-toxic seawater system. Phytoplankton samples for the single-cell flavodoxin assay will be pre-concentrated onboard ship and later analysed shoreside.

Sampling will be conducted by:

- towed batfish with a clean pump and tubing (this is not a pumping undulating fish): conductivity/salinity sensor, SF_6, fCO_2, pH, nitrate, iron, Chlorophyll *a* (fluorometer) (measurments will be sampled continuously);
- hydrocasts by rosette CTD/Niskin samplers: T, S, O_2, Chlorophyll *a*, macronutrients (N, P, Si) by auto-analyzer, iron by chemiluminescence, particulate iron size-fractions, total iron, dissolved iron, SF_6, DIC, TA, pH, DOC, DON, POC, DMS;
- free-drifting sediment traps (at 50-m intervals, 50–600 m) deployed and retrieved at 3-day intervals to obtain samples for detritus organic C, N, P, Si, PIC, Fe, Cd, Al, rare earth elements, Th:U ratios, coccolithophore counts and planktonic species, and scanning electron microscope pictures;
- deckboard perturbation experiments: algal carbon, growth rates and C:Chl-*a* ratios, *etc*.

We (Drs. C.S. Wong and Paul J. Harrison) hope to have one or two strings of moored sediment traps, plus free floating traps. Moored traps would be at the control site. Floating traps would hopefully follow the patch. It will be difficult to keep the patch and traps together, but there is a real need for trap data to try to quantify and characterize export. Free-floating sediment traps may perform differently than moored traps. Therefore, we should have free-floating traps in and out of the iron patch. There is a need to know more about microzooplankton, the effects of ligands, and also climate change biogases, including but not limited to, DMS, CO_2, and N_2O. SOIREE showed enhancement of nitrous oxide at the top of the thermocline, so this is one gas that should be studied. There will be aircraft-based sampling of gases and aerosols above the iron patch. We hope to sample over a longer time, possibly by back-to-back cruises extending over 6 weeks. We expect to have the CCGS *J.P. Tully* for 4 weeks and will need another ship for one of these two cruises. Cruises could be separated by several weeks if the patch could be found on second cruise. Iron limitation at Station P in July and August is severe, so the project will need to take place during this time. The project will be part of the Canadian SOLAS program.

Summary of the Japanese programs

A preliminary experiment of about 40 days is proposed during June–August 2001 on board the R/V *Kaiyo-Maru* in the WSG (45–50°N, 160–165°E), with next effort in August to mid-September 2003 with the T/S *Oshoro-Maru* or R/V *Kaiyo-Maru*) to initiate the SF_6/Fe patch and conduct the basic study. In October 2003 the R/V *Hakuho-Maru* will be used for intensive sampling and measurements. From analyzing long-term responses, we hope to:

- measure responses of bacteria, phytoplankton and zooplankton in terms of species, standing stocks and rate processes to the iron addition;
- measure the drawdown of CO_2 and the flux of carbon export;
- study the interaction between biogeochemical processes in the surface water during the phytoplankton bloom and the production of climate gases in the atmosphere;
- study the relationship between phytoplankton (diatom) production and higher trophic levels (salmon);
- assess the influence of iron supply on the characteristics of the plankton ecosystem in the western subarctic Pacific.

Proposals will be submitted to the Science and Technology Agency (2001–2005), Ministry of Education, Science and Culture (2001 Basic Science, 2002–2004 Scientific project with high priority) and NEDO grant.

A1.1.2 Discussions on experimental design

What do we know from IronEx I and IronEx II and SOIREE, *etc.*?

Japan SOLAS is still in the preparation stage. A study of the influence of natural atmospheric iron supply on the characteristics of the plankton ecosystem in the western subarctic Pacific will be one of the important topics. (A long cruise is expected to stay at a station in the spring high dust season.)

- Iron limitation is clearly present in populations of phytoplankton in HNLC regions.
- Iron enrichment de-couples larger phytoplankton from the mesozooplankton community.
- Evidence for carbon export in SOIREE is not clear. There may have been an export of carbon, yet a retention of iron. Evidence for carbon export in IronEx is clearer.
- The response rate in SOIREE was much slower than that in IronEx.
- There is now more interest in the effect of iron enrichment in different macronutrient-limited regimes, specifically low NO_3 where N-fixation dominates N-uptake.
- A ship-based study of light limitation of iron enrichment in the SOIREE region showed that light limitation is present at 100 m.
- There is some interest in long-term addition experiments using low levels of iron.
- The role of mesoscale eddies at Station P is intriguing. They may offer a way to track a patch of water for years, but the phytoplankton community in an eddy may be untypical of the Gulf of Alaska. Also, eddies have no surface water expression, so their relevance to an iron enrichment experiment is not clear.
- The European community has just sent (November 2000) the R/V *Polarstern* to the Southern Ocean (in the Atlantic sector) to do a SOIREE-type experiment over a longer time, such as the **CAR**bon Dioxide **U**ptake by the **S**outhern **O**cean (CARUSO) experiment.

What do we still need to know?

- There is a need to study Station P, and the NW Pacific, but other regions need to be studied too.
- What is the fate of primary production (carbon) on POC export flux, DOC, respiration and response of higher trophic levels (is there an increase in fish production?). The time scale is over a year, so a model approach is needed.
- What are the roles of ligands? What members of the community produce and take up ligands?
- Does zinc affect other enzyme processes?
- There is a need to study DMS/DMSP and other climate change biogases. Previous iron enrichment studies have measured DMS production. There should be both ships and aircraft for sampling. At Station P, ocean levels of DMS are very high; atmospheric levels are low.
- We need to know what factors influence the carbon-to-nutrient and other trace metal export ratios.
- Iron might end up below the mixed layer during long-term commercial projects. Will it become available the next summer after winter mixing?
- Would long-term iron enrichment drive a system toward another limitation (N, Si, Zn, Co, *etc.*)?
- What is the impact of long-term iron enrichment on fish? Governments may see fish production as a secondary benefit of iron enrichment, so this question will be asked of us. The public may see this as a problem, due to “wrong” species benefiting, such as pennate diatoms that produce domoic acid. (These are not questions that can be addressed with the current experiment.)
- What are the chemical processes associated with iron saturation and super-saturation of seawater?
- How does Fe(II) stay around so long in iron enrichment patches?
- What are the major grazers on diatoms and how do they respond when diatom (pennate/centric) abundance increases?
- Understanding the dynamics of the plankton ecosystem, export carbon flux and climate-related gases to iron enrichment is appropriate for the requests of Government and Industry who are seeking scientific information to asses the effects on future global atmospheric CO_2 and environmental impacts.

What do we hope to learn from an iron enrichment experiment at Station P and WSG?

- What are the similarities and differences in the plankton ecosystem response to iron fertilization in the subarctic Pacific?
- There is a special interest in the east–west North Pacific comparison which includes differences in dominant species (pennate/centric diatoms) and export flux (Org-C/Opal/$CaCO_3$).

Methodology

- There is a need to standardize sampling methods to enable comparison among experiments in different HNLC regions. A list of dominant species and their biomass is useful for the comparison.
- The first step is the application of previous IronEx methodology ($FeSO_4$, initial concentration level, iron infusion timing, *etc.*). Then we may go to a new method such as the use of chelated iron (iron lignite), long-period and low-level iron supply, *etc*.
- We should add DMSP to list of samples.
- Microzooplankton are important grazers and dilution experiments are necessary to quantify the coupling of primary production and grazing.
- Iron organic ligand studies have technical problems but how are they to be solved?
- Analyses of biogases in the atmosphere are important, but how are they to be done?
- Bag experiments have limitations. Small bags might not represent the ocean. Large bags are too difficult to manage. However, there should be some role for bag experiments.
- The use of organic chelated iron (iron lignite) may provide carbon source for heterotrophic organisms.
- A stable isotope study will be done in SOFeX to see the proxy of the paleo-oceanographic environment.
- After silicate in the surface water will be used up, a re-infusion of iron will give us some idea of the long-term change in dominant species.

Logistics

- The Station P project needs a second ship. Kenneth Coale recommended that a U.S. ship may be available if a group of American scientists were to propose to participate. The U.S. SOLAS program would be one way to generate support. It would help to have a Canadian–Japanese proposal ready. U.S. scientists must start to prepare proposals now for the Station P 2002 cruise.
- Canadian or U.S. aircraft would be useful for tracking the iron patch. An airplane with a hyperspectral sensor would be really helpful.
- ADIOS-2 will be launched soon. Similar to SeaWiFS, it will be useful.

A1.2 EXTENDED ABSTRACTS OF THE 2000 IFEP PLANNING WORKSHOP

A1.2.1 General overview of IronEx and SOIREE, iron chemistry and biology in seawater

Open ocean iron fertilization for scientific study and carbon sequestration

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Abstract

Through initial enrichment experiments in the subarctic Pacific and a series of recent large-scale iron fertilization experiments in the equatorial Pacific and the Southern Ocean, strong correlations in atmospheric iron deposition, marine production and climate change have now been mechanistically linked to iron limitation in the global ocean. These experiments have been significant in a number of ways: (1) they have advanced the importance of iron in regulating phytoplankton production on global scales, (2) they have demonstrated the utility of open ocean enrichment experiments for the study of ecological and physiological processes, and (3) they have suggested that anthropogenically induced eutrophication through open ocean iron fertilization may be useful in controlling atmospheric carbon dioxide. Although the latter remains an issue of current study and debate, the utility of iron fertilization in examining a variety of biological and geochemical processes has been unequivocally demonstrated.

The ability to perform such experiments, however, is not trivial and involves many demanding capabilities. Here, we report the theoretical and practical considerations of creating a patch of seawater enriched with iron, then detecting this patch and the biological and chemical signal which developed, in an area dominated by advective processes. Physical and chemical models were used to predict the speciation, solubility, and the final concentration of iron in surface waters injected with acidic iron sulfate. A Lagrangian coordinate system was established using a drogued buoy, and the iron-enriched area was tagged with the inert chemical tracer sulfur hexafluoride (SF_6).

This method has proven useful on four experiments conducted by Moss Landing Marine Laboratories (MLML) researchers in the equatorial Pacific and in the Southern Ocean. Shipboard analysis and airborne observations confirmed good spatial agreement between the Lagrangian drifter and the biological and chemical signatures in the patch.

The biological response, upon addition of iron to high nitrate, low chlorophyll (HNLC) systems, is becoming more predictable. Although the inert tracer allows for an estimate of the physical mixing of the enriched waters, a well constrained budget of carbon export is more difficult to calculate.

Experimental strategy

The mechanics of producing an iron-enriched experimental patch and following it over time has been worked out in four release experiments in the equatorial Pacific (IronEx I and II, Martin *et al.*, 1994; Coale *et al.*, 1996) and more recently in the Southern Ocean (SOIREE, Boyd *et al.*, 2000). A similar strategy will be employed in the CARUSO (**CAR**bon Dioxide **U**ptake by the **S**outhern **O**cean) experiments now underway in the Atlantic sector of the Southern Ocean and will be similar to the methods used by the SOFeX (Southern Ocean Iron Experiment) group in an upcoming experiment.

Form of iron

Based upon the IronEx experiments, these all involve the injection of an iron sulfate solution into the ship's wake where it is rapidly diluted and dispersed throughout the mixed layer. The rationale for using ferrous sulfate is given in Coale *et al.* (1998) and involves the following thinking: (1) Ferrous sulfate is the most likely form of iron to enter the oceans via atmospheric deposition, (2) it is readily soluble (initially), (3) it is available in a relatively pure form so as to reduce the introduction of other potentially bioactive trace metals and

(4) its counter ion (sulfate) is ubiquitous in seawater and not likely to produce confounding effects. Although mixing models indicate that iron (II) carbonate may reach insoluble levels in the ship's wake, rapid dilution reduces this possibility.

New forms of iron are now being considered by those who would seek to reduce the need for subsequent infusions. Our laboratory has investigated the bioavailability of iron lignosite to phytoplankton in the California Current. These results indicate that, on an equimolar basis, iron lignosite may be as effective or better in promoting phytoplankton growth. Because this is a chelated form of iron, problems of rapid precipitation are reduced. In addition, Fe-lignosite is about 15% Fe by weight making it a space-efficient form of iron to transport. As yet untested is the extent to which such a compound would reduce the need for re-infusion.

Inert tracer

Concurrent with the injection of iron is the injection of the inert chemical tracer, SF_6. By presaturating a tank of seawater with SF_6 and employing an expandable displacement bladder, a constant molar injection ratio of Fe:SF_6 can be achieved. In this way, both conservative and non-conservative removal of iron can be quantified. In addition, the relatively rapid shipboard detection of SF_6 can be used to track and map the enriched area (Upstill-Goddard *et al.*, 1991; Watson *et al.*, 1991). Addition of Helium-3 to the injected tracer can provide useful information regarding gas transfer. These experiments have been further developed (Law *et al.*, 1998; Nightingale *et al.*, 2000).

Fluorometry

Because the biophysical response of the phytoplankton is rapid and readily detectable, shipboard measurements of relative fluorescence (F_v/F_m) using fast repetition rate (FRR) fluorometry is a useful tactical tool and gives nearly instantaneous mapping and tracking feedback (Greene *et al.*, 1991; Kolber *et al.*, 1994; Behrenfeld *et al.*, 1996).

Shipboard iron analysis

Because iron is rapidly lost from the system (at least initially), the shipboard determination of iron is necessary to determine the timing and amount of subsequent infusions. Several shipboard methods, using both chemiluminescent and catalytic colorimetric detection have proven useful in this regard (Elrod *et al.*, 1991; Obata *et al.*, 1993; Johnson *et al.*, 1994).

Lagrangian drifters

A Lagrangian point of reference has proven to be very useful in every experiment to date. Depending upon the advective regime, this is the only practical way to achieve rapid and precise navigation and mapping of the enriched area (Stanton *et al.*, 1998).

Remote sensing

A variety of airborne and satellite-borne active and passive optical packages provide rapid, large-scale mapping and tracking of the enriched area (Hoge *et al.*, 1998). Although SeaWiFS was not operational during IronEx I and II, AVHRR was able to detect the IronEx II bloom and airborne optical LIDAR was very useful during IronEx I. SOIREE (**S**outhern **O**cean **IR**on **E**nrichment **E**xperiment) has made good use of the more recent SeaWiFS images which have markedly extended the observational period and led to new hypotheses regarding iron cycling in polar systems (Abraham *et al.*, 2000).

What we (think we) know

Biophysical response

The experiments to date have focused on the HNLC areas of the world's oceans, primarily in the subarctic, equatorial Pacific and Southern Ocean. In general, when light is abundant many researchers find that HNLC systems are iron limited. The nature of this limitation is similar between regions but manifests itself at different levels of the trophic structure in some characteristic ways. In general, all members of the HNLC photosynthetic community are physiologically limited by iron availability. This observation is based primarily on the examination of the efficiency of photosystem II, the light-harvesting reaction centers. At ambient levels of iron, light harvesting proceeds at sub-optimal rates. This has been attributed to the lack of iron-dependent electron carrier proteins at low iron concentrations. When iron concentrations are increased by

sub-nanomolar amounts, the efficiency of light harvesting rapidly increases to maximum levels. Observations using FRR fluorometry and non-heme iron proteins have been described in detail (Greene *et al.*, 1991; Kolber *et al.*, 1994; Behrenfeld *et al.*, 1996; La Roche *et al.*, 1996). What is notable about these results is that iron limitation seems to affect the photosynthetic energy conversion efficiency of even the smallest of phytoplankton (Cavender-Bares *et al.*, 1999). This has been a unique finding which stands in contrast to the hypothesis that, because of diffusion, smaller cells are not iron limited, but larger cells are.

Nitrate uptake

Iron is also required for the reduction (assimilation) of nitrate. In fact, a change of five oxidation states is required between nitrate and the reduced forms of nitrogen found in amino acids and proteins. Such a large and energetically unfavorable redox process is only possible by substantially reducing power (in the form of NADPH) made available through photosynthesis (see above) and active nitrate reductase, an iron-requiring enzyme. Without iron, plants cannot take up nitrate efficiently. This provided original evidence implicating iron deficiency as the cause of the HNLC condition. When phytoplankton communities are relieved from iron deficiency, specific rates of nitrate uptake increase. Cochlan *et al.* (2002) have observed this in both the equatorial Pacific and the Southern Ocean using isotopic tracers of nitrate uptake and conversion.

Growth response

When relieved from resource-based physiological limitation, phytoplankton growth rates increase dramatically (Coale *et al.*, 1996; Fitzwater *et al.*, 1996). In several experiments, over widely differing oceanographic regimes, we have demonstrated that when light and temperature are favorable phytoplankton growth rates in HNLC environments increase to their maximum at dissolved iron concentrations generally below 0.5 nM. This observation is significant in that it indicates that phytoplankton are adapted to very low levels of iron, that is, they do not grow faster if given more than half a nanomolar of iron. Given the disagreement within the scientific community about the validity of iron measurements, these phytoplankton provide a natural environmental and biogeochemical benchmark against which to compare results.

Heterotrophic community

As the primary trophic level producers, it appears that these consumers of recently fixed carbon (both particulate and dissolved) respond to the food source and not necessarily to the iron. Because their division rates are fast, heterotrophic bacteria, ciliates and flagellates can rapidly respond to increasing food availability to the point where the growth rates of the smaller phytoplankton can be almost balanced by grazing (Barbeau *et al.*, 1996; Hall and Safi, 2001). Thus there is a much more rapid turnover of fixed carbon and nitrogen in iron-replete systems. Landry *et al.* (2000) have documented this in dilution experiments conducted during IronEx II. These results also appear to be consistent with the recent SOIREE experiments.

Nutrient uptake ratios

An imbalance in production and consumption, however, can arise at the larger trophic levels. Because the reproduction rates of the larger micro- and mesozooplankton are long with respect to diatom division rates, iron-replete diatoms can escape the pressures of grazing on short time scales (weeks). This is thought to be the reason why, in every iron enrichment experiment, diatoms ultimately dominate in biomass. This result is important for a variety of reasons. It suggests that transient additions of iron would be most effective in producing net carbon uptake and it implicates an important role of silicate in carbon flux. The role of iron in silicate uptake has been studied extensively by Franck *et al*. (2000). Our results, together with those of Takeda and Obata (1995), show that iron alters the uptake ratio of nitrate and silicate at very low levels.

Organic ligands

Consistent with the role of iron as a limiting nutrient in HNLC systems is the notion that organisms may have evolved competitive mechanisms to increase iron solubility and uptake. In terrestrial systems this is accomplished using extracellularly excreted or membrane-bound siderophores. Similar compounds have been shown to exist in seawater where the competition for iron may be as fierce as it is on land. In open

ocean systems where it has been measured, iron-binding ligand production has increased with the addition of iron. Whether this is a competitive response to added iron or a function of phytoplankton biomass and grazing is not yet well understood. However, this is an important natural mechanism for reducing the inorganic scavenging of iron from the surface waters and increasing iron availability to phytoplankton. Several studies (Trick and Wilhelm, 1995; Van den Berg, 1995; Rue and Bruland, 1997; Croot *et al.*, in prep.) have advanced considerably our understanding of these ligands, their distribution and their role in ocean ecosystems.

Carbon flux

It is this imbalance in the community structure which gives rise to the geochemical signal. Whereas iron stimulation of the smaller members of the communtures, such as an increased production of dimethylsulfionproprionate (DMSP) occurs (Turner *et al.*, 1996), it is the stimulation of the larger producers which decouples the large cell producers from grazing and results in a net uptake and export of nitrate, CO_2 and silicate. The extent to which this imbalance results in carbon flux, however, has yet to be adequately constrained. This has been primarily a problem of experimental scale. Even though mesoscale experiments have, for the first time, given us the ability to address the effect of iron on communities, the products of surface water processes have been difficult to track. For instance, on the IronEx II experiment, a time series of the enriched patch was diluted by 40% per day and is described by Nightingale *et al.* (2000). The dilution was primarily in a lateral (horizontal/isopycnal) dimension. Although some correction for lateral dilution can be made, our ability to quantify carbon export is dependent upon the measurement of a signal in waters below the mixed layer, or from an uneroded enriched patch. Current data from the equatorial Pacific showed that the IronEx II experiment advected over six patch diameters per day. This means that at no time during the experiment were the products of increased export reflected in the waters below the enriched area. Our results from the equatorial Pacific, when corrected for dilution, suggest that about 2,500 tons of carbon were exported from the mixed layer over a 7-day period. These results are preliminary and subject to more rigorous estimates of dilution and export production, but they do agree favorably with estimates based upon both carbon and nitrogen budgets.

Experimental scale

Given these considerations, the most feasible way to understand and quantify carbon export from an enriched water mass is to increase the scale of the experiment such that both lateral dilution and sub-mixed layer relative advection is small with respect to the size of the enriched patch. For areas such as the equatorial Pacific, this would be very large (100s of kilometers on a side). For other areas, this could be much smaller. From the acoustic Doppler current profiler (ADCP) data presented, it appears that lateral advection was not as much of a problem during SOIREE as during the IronEx experiments. The relative advection of the enriched patch over the underlying waters will be a function of wind stress and regional hydrodynamics. In the subarctic Pacific, this can be severe. It is this author's opinion that an uncontained enrichment experiment in this region should be large (1000 km^2 or greater) to avoid lateral mixing and slippage relative to the sub-mixed layer.

What we need to know

There are a multitude of questions remaining regarding the role of iron in shaping the nature of the pelagic community. Some of these topics involve the role of the heterotrophic bacterial community in cycling iron and carbon, the extent to which the smaller phytoplankton contribute to flux, the partitioning of light isotopes of carbon and nitrogen in biomarker compounds and in the bulk plankton and their use in establishing paleo-isotopic tracers of growth rate and trophic structure, the use of single cell FRR fluorometry to study species specific response to iron, the use of sediment traps and radioisotopic disequilibrium to measure and infer carbon export. Many of the remaining questions will be the subject of the CARUSO and SOFeX experiments as well as future experiments in the subarctic Pacific. The focus of the IronEx and SOFeX experiments has been from the scientific perspective, but this focus is shifting towards the application of iron enrichment as a carbon sequestration strategy. We have come about rapidly from the perspective of trying to understand how the world works, to one of trying to make the world work for us.

Several basic questions remain regarding the role of natural or anthropogenic iron fertilization on carbon export. Some of the most pressing questions are: What are the best proxies for carbon export? How can carbon export best be verified? What are the long term ecological consequences of iron enrichment on: (1) surface water community structure? (2) midwater processes? (3) benthic processes? And what is the response of the community structure and biological pump to iron enrichment in low nutrient low chlorophyll (LNLC) systems where nitrogen fixation may be iron limited? Even with these answers, there are others which would need to be addressed prior to any serious consideration of iron fertilization as an ocean carbon sequestration option (see below).

Technology

Simple technology is sufficient to produce a massive bloom. The technology required for either a large-scale enrichment experiment or for purposful attempts to sequester carbon, is readily available. Ships, aircraft (tankers and research platforms), tracer technology, a broad range of new AUVs (autonomous underwater vehicles) and instrument packages, Lagrangian buoy tracking systems, together with aircraft and satellite remote sensing systems and a new suite of chemical sensors/*in situ* detection technologies are all available, or are being developed at this time. The big questions, however, are larger than the technology.

Resources

With a slow start, the notion of both scientific experimentation through manipulative experiments, as well as the use of iron to purposefully sequester carbon, is gaining momentum. There are now national, international, industrial, and scientific concerns willing to support larger-scale experiments. The materials required for such an experiment are inexpensive and readily available even as industrial byproducts (paper, mining, steel processing).

Feasibility

Given the concern over climate change and the rapid modernization of large underdeveloped countries (China, India, *etc.*), there is a pressing need to address the increased emission of greenhouse gasses. Through the implementation of the Kyoto accords or other international agreements to curb emissions (Rio), financial incentives will reach into the multi-billion dollar level annually. Certainly there will soon be an overwhelming fiscal incentive to investigate, if not implement purposeful open ocean carbon sequestration trials.

Questions

The question is not whether we have the capability of embarking upon such an engineering strategy, the question is whether we have the collective wisdom to responsibly negotiate such a course of action. Posed another way: If we do not have the social, political and economic tools or motivation to control our own population and greenhouse gas emissions, what gives us the confidence that we have the wisdom and ability to responsibly manipulate and control large ocean ecosystems without propagating yet another massive environmental calamity? Have we, as an international community, first tackled the difficult but obvious problem of overpopulation and implemented alternative energy technologies for transportation, industry and domestic use?

There are other social questions which arise as well, such as: Is it appropriate to use the ocean commons for such a purpose? What individuals, companies or countries would derive monetary compensation for such an effort and how would this be decided?

It is clear that there are major science investigations and findings which can only benefit from large-scale open ocean enrichment experiments, but certainly a large-scale carbon sequestration effort should not proceed without a clear understanding of both the science and the answers to the questions above.

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Dissolved iron speciation in seawater

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Introduction

The role of iron in limiting oceanic productivity and influencing community structure has been demonstrated for the high nitrate, low chlorophyll (HNLC) waters of the subarctic Pacific, equatorial Pacific, the Southern Ocean, and even some coastal upwelling regimes. As a consequence, iron has been elevated to the same status as nitrogen, phosphorus and silicon as important nutrients influencing global biogeochemical cycles. In oceanic surface waters, concentrations of dissolved iron (defined as the iron concentration in the filtrate passing through a conventional 0.2 or 0.4µm filter) commonly range from 0.02 nM (20 pM) to 1 nM. In remote HNLC regimes (such as the equatorial Pacific, subarctic Pacific, and parts of the Southern Ocean) iron can be a limiting nutrient with dissolved iron concentrations in surface waters on the order of 0.02 to 0.05 nM (20 to 50 pM). These concentrations are low enough for dissolved iron to be diffusion limiting with respect to growth rates for all but the smallest phytoplankton cells (Hudson and Morel, 1990; Sunda and Huntsman, 1995). Measurements of total dissolved iron concentrations alone, however, are insufficient for understanding the accessibility of iron to phytoplankton. Knowledge of the chemical speciation of iron is critical for examining the mechanisms by which phytoplankton are fulfilling their iron requirements and is important for addressing the question of how the lack of iron limits phytoplankton productivity in certain regions of the oceans.

Discussion

The majority of this dissolved iron in remote low-iron, HNLC regimes appears to be chelated (as FeLi) with organic ligands (Li) which resemble siderophores in their conditional stability constants and molecular weight (Rue and Bruland, 1997). In HNLC areas such as the equatorial Pacific, it appears that these chelated forms of iron are primarily less than 1000 in relative molar mass (molecular weight) (Rue and Bruland, 1997), with only a small fraction existing as larger, colloidal size material. In these low-iron waters, both Li and FeLi appear to exist primarily in the soluble fraction and colloidal forms do not appear to be a significant fraction of the dissolved iron. Results on the chemical speciation of iron in central gyre regions of the North Pacific and North Atlantic both indicate that the bulk of the dissolved iron exists as organic Fe(III)-chelates (Rue and Bruland, 1995; Wu and Luther, 1995). Even though the data are very limited, it even appears that iron in the deep ocean exists primarily as Fe(III)-chelates (Rue and Bruland, 1995; Nolting *et al*., 1998) although it is uncertain to what extent the iron is soluble or colloidal in form. The higher concentrations of dissolved iron in coastal waters also appear to be associated with organic ligands (Gledhill and van den Berg, 1994; van den Berg, l995). In contrast to the low-iron open ocean, however, the high-iron Narragansett Bay (Rhode Island, United States) has the bulk of what seems to be organically complexed dissolved iron existing as a colloidal Fe fraction, with only a small amount found in the relative molar mass <1000 ultrafiltrate (Rue and Bruland, pers. comm.). Powell *et al*. (1996) used ultrafiltration to carry out a size-fractionation study of dissolved iron and dissolved organic carbon in the Ochlockonee estuary (Florida, United States). They showed that in high-iron, low-salinity regions of the estuary the vast majority of iron was in the high molecular weight fraction (relative molar mass >10,000), but that this component was only a minimal fraction in higher salinity regions. Thus, the chemical form of dissolved iron appears to change dramatically from being primarily associated with a complex, higher molecular weight, colloidal fraction in estuarine and fresh waters, to being in the form of low molecular weight, water soluble, strong Fe(III)-organic chelates in oceanic surface waters.

Although the identity, origin, and chemical characteristics of these organic compounds are largely unknown, it has been implied that some

component of these natural ligands are siderophores (Rue and Bruland, 1995). Macrellis *et al*. (2001) report the first direct evidence from natural seawater to support this theory. Large volume seawater collection and solid phase extraction employing Biobeads SM-2 and Amberlite XAD-16 resins were conducted in the California coastal upwelling system. Electrochemical analyses using competitive ligand equilibration/adsorptive cathodic stripping voltammetry (CLE-ACSV) showed that extracted groups of compounds had conditional iron-binding affinities (with respect to Fe') of $K^{cond}_{FeL,Fe'}$ = $10^{11.5}$–$10^{11.9}$ M^{-1}, identical to those constants measured for purified marine siderophores produced in laboratory cultures. In addition, 63% of the extracted compounds fall within the defined size range of siderophores (300–1000 Daltons). Hydroxamate or catecholate iron-binding functional groups were responsible for iron complexation in all isolated extracts, illustrating that the functional groups previously shown to be active in marine and terrestrial siderophores extracted and purified from laboratory cultures are active in a natural marine community milieu. Thus, these data provide the first evidence from natural marine systems that a significant fraction of the organic iron-binding compounds that control the availability of iron and therefore, influence the global biogeochemical cycling of this micronutrient, are biologically produced siderophores.

Much of the current interest in the marine chemistry of iron stems from its role as a limiting micronutrient affecting plankton productivity and biological species composition. The high degree of organic complexation of iron makes it critically important to re-evaluate our perceptions of the marine biogeochemistry of iron and the mechanisms by which biota can access this chelated iron. Trace metal assimilation by phytoplankton has historically been modeled using the free ion concentration (or activity) model (Morel and Hering, 1993), with iron uptake by phytoplankton typically correlated with free, hydrated Fe^{3+} concentrations (using EDTA buffered solutions). It is now realized, however, that it is the far more abundant, kinetically labile, hydrolysis species comprising Fe(III)' (such as $Fe(OH)^{2+}$) that actually control uptake rates of inorganic iron (Hudson and Morel, 1990; Hudson, 1998). As a result, recent papers dealing with iron limitation in laboratory culture media correlate effects with [Fe(III)'] rather than [Fe^{3+}] (Sunda and Huntsman, 1995).

A recent example (Rue and Bruland, 1997) of an iron speciation study in a low-iron HNLC area was performed as part of the IronEx II mesoscale iron addition experiment (Coale *et al*., 1996). Rue and Bruland (1997) observed two classes of Fe(III)-binding organic ligands: a strong ligand class (L1) with a conditional stability constant $K^{cond}_{FeL1,Fe(III)'}$ = 5×10^{12} L mol^{-1} and a mean concentration of 310 pM, and a weaker class (L2) with a conditional stability constant $K^{cond}_{FeL2,Fe(III)'}$ = 6×10^{11} L mol^{-1} and a mean concentration of 190 pM. The total Fe(III)-binding organic ligand concentrations were ~25 times higher than total dissolved iron concentrations of only 20 pM. Thermodynamic equilibrium calculations suggest that 99.9% of the ambient dissolved Fe(III) would be complexed with these organic ligands and results from ultra filtration experiments indicated that they exist as low molecular weight Fe(Ill) chelates. Upon the initial mesoscale iron injection of ~2nM, the total iron-binding ligand concentration increased by 400% to 2 nM within a day. Most of this increase was due to the stronger ligand class, L1, which increased from 0.3 to 1.3 nM. Results obtained from samples collected throughout the entire course of the iron enrichment experiments suggest that these iron-binding organic ligands are produced rapidly in response to small iron additions to this low-iron regime. The chelated iron appears to somehow be directly or indirectly accessible for growth. The presence of these chelators causes the labile inorganic species (Fe(III)') to exist at extremely low concentrations, perhaps requiring photochemical or other redox mechanisms to provide an adequate supply of Fe' (Rue and Bruland, 1997; Price and Morel, 1998). At this point, we are just beginning to understand how chelated iron might be accessible by the biological community (Maldonado and Price, 1999, 2000; Wells and Trick, 2004). Prokaryotes and even unicellular eukaryotes, such as diatoms, appear to be able to utilize some of the chelated iron (Price *et al*., 1994; Price and Morel, 1998; Hutchins *et al.*, 1998, 1999). There are suggestions that eukaryotic phytoplankton, such as diatoms, can access this chelated Fe(III) by using cell surface-bound reductases to reduce the chelated Fe(III) to Fe(II) which then dissociates and is subsequently assimilated either as Fe(II)' or, after

re-oxidation, as Fe(Ill)' (Maldonado and Price, 1999). There are some data to suggest that the protozoan grazers of the microbial community can utilize and solubilize colloidal iron (Barbeau *et al*., 1996), and there is also evidence that particulate iron associated with the plankton community can be remineralized and reused as regenerated iron much in the same way as nitrogen is recycled (Hutchins *et al*., 1993; Hutchins and Bruland, 1994). Price and Morel (1998) estimated that 83% of the iron uptake by microorganisms within the euphotic zone of the equatorial Pacific was from such biological regeneration, while the remaining 17% was supplied from external sources such as eolian deposition and upwelling. In addition, it has been suggested that various members of the phytoplankton and microplankton community can utilize phagocytosis to engulf and partially digest particulate iron (Raven, 1997), thereby rendering a fraction of the particulate iron available over an extended time scale. Recent evidence suggests that the photosynthetic phytoplankton *Ochromonas* can obtain iron directly in particulate form by ingesting bacteria (Maranger *et al*., 1998). As a result of the diversity of iron uptake strategies employed by various marine microorganisms, some of the "non-available" iron is likely recycled by various mechanisms and at various rates into biologically available forms (Wells and Mayer, 1991; Wells *et al*., 1995). Therefore, most of the dissolved iron and part of the particulate iron may eventually be made available to the plankton community.

Conclusions

Addressing the processes responsible for the role of iron forces us to look more closely at its marine chemistry. The majority of dissolved iron exists as Fe(III)-chelates with relatively specific and strong Fe(III)-binding ligands. Results from iron fertilization experiments have raised a number of questions that point to the need for more research. What are these iron-binding ligands? Are the stronger class of ligands, apparently produced in rapid response to increased iron levels, siderophores? Are they inducible, excreted, and regulated? What about the weaker class of ligands? Are these simply photochemical degradation products or cell lysis products (from zooplankton grazing or viral lysing) containing porphyrin groups such as those in cytochromes, chlorophylls, and haem proteins? Very little information exists, however, as to the chemical nature of these iron-binding ligands or the mechanisms involved in their production, function or fate. The need for future research elucidating the molecular structure and character of the strong iron-binding ligands observed in seawater has been recognized and has begun. In addition, research into the biological availability of the various chelated forms of iron, and the mechanisms various microorganisms utilize to access these iron species, will continue to be a research area of great importance in the next decade.

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Fundamental differences in the iron acquisition systems among phytoplankton

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Abstract

Laboratory and shipboard "grow-out" experiments have provided the foundation of our understanding of how different members of the phytoplankton community access "free iron" versus iron bound in natural or artificial ligands. While the mechanism(s) is not fully established, these laboratory and natural population experiments have provided insights into how different members of a community compete for iron supplied either as a xenosiderophore–iron complex or as a ligand–iron complex. We make the distinction between known siderophores added to the system (xeno-siderophores, in this case) and the natural ligands that have been isolated and/or described by the van den Berg and Rue/Bruland research groups. To investigate the role of each of these iron–organic complexes on the shaping of the phytoplankton community, natural populations were exposed to increasing levels of organic iron complexing agents during three recent cruises. The growth and composition of the population were monitored to assess the impact of individual ligands on the eukaryotic and prokaryotic communities. Flow cytometric analysis offered unique insights into the effects of a range of levels of available iron on the phytoplankton community from contrasting oceanographic regimes, including high nutrient, low chlorophyll (HNLC) areas and the oligotropbic central gyres.

Introduction

There are two dichotomies that must be considered when evaluating the methods by which natural phytoplankton communities acquire iron. First, there is a dichotomy on how we view the different population "adaptations". Second, how do we view the source material — the form of iron? The most important question in assessing the relationship between the cellular physiological processes with the ecological processes is based on how we combine these two dichotomies.

In the traditional cellular view, the accessibility of specific forms of iron is different between the two most prominently discussed groups of phytoplankton: the cyanobacteria and the diatoms. Considerable research on the iron acquisition system by diatoms clearly indicates that the prime form of available iron is that of the free ionic form (often referred to as Fe'). When physiologically available forms of iron are reduced to a specific level, the cell accommodates with alterations in the cell quota for iron (by altering the cellular composition: reduction in the iron demands in the photosystem (ferridoxin:flavodoxin), reducing the demands for iron in chlorophyll biosynthesis, perhaps reducing the iron demands for nitrate acquisition). All of these changes occur in direct response to the level of Fe'.

In contrast, the physiological status of cyanobacteria is equally dependent on the availability of free inonrganic iron (Fe') until the levels of iron are reduced significantly to induce the low-iron physiology of these cells. The low-iron physiological state induces a slight reduction in the iron quota of the cell, but the magnitude of the change is not as pronounced as in the diatom model. The primary alteration in cell physiology when Fe' is low is the induction (through depression) of the high-affinity iron acquisition system. This system is a two (or more) part acquisition system comprising of an extracellular-released iron binding ligand (termed: siderophore) and the equally specific iron–ligand membrane receptor for the transport of the ligand-bound iron.

From the cellular perspective, we can refer to these as the FIT (Free Iron Transport) model and the LIT (Ligand Iron Transport) model and we note that our view of iron availability in the oceans in many ways now parallels these two models. Rue and Bruland (this workshop) have just outlined the importance of the naturally formed ligands in marine waters in comparison with the level of newly advected or introduced iron within an ecosystem. Thus, how iron is provided in an

ecosystem is the next dichotomy: some systems are dominated by "fresh" inorganic iron (paralleling the FIT model) whereas others have significant levels of natural ligand binding the iron (paralleling the LIT model). The origin of this natural ligand remains unknown but appears to be a collection of potentially active compounds (Macrelis *et al*., 2001).

In this presentation I would like to propose whether we are accurate in implying the ecological and physiological descriptions of the FIT and LIT models hold true, based on our laboratory and shipboard grow-out experiments. For this presentation I will limit myself to the use of the addition of artificial ligands. In this case, the artificial ligands are siderophores produced by, and isolated from, microorganisms other than the ones we are studying in these experiments. I will use the term "xenosiderophore" to denote these ligands since they are produced in response to iron stress by the host cell ("siderophore") that is foreign ("xeno") to the ecosystem. I will consider the influence of two xenosiderophores on four phytoplankton cultures and on natural communities from a HNLC region of the Eastern Pacific Ocean.

Materials and methods

Laboratory experiments

Experiments were performed in the laboratory using the following cultures: *Synechococcus* sp. PCC7002, *Talassiosira weissflogii* CCMP1051, *Heterosigma akashiwo* NEPCC560R, and *H. akashiwo* NEPCC764R. All cells were maintained in four separate modifications of artificial seawater (ASM) (Harrison *et al.*, 1980) supplemented with f/2 nutrients, metals (except iron) and vitamins. Cells were maintained at four different levels of iron ranging from 0.1 μM to 1 μM. Cells were grown at l8ºC under continuous light flux of 65–80 μmol photons m^{-2} s^{-1}.

The batch culture experiments of 50 mL cultures were prepared in 250 mL acid-washed Erlenmeyer flasks. Cultures were preconditioned in the appropriate medium using the stock culture maintained at the nearest iron concentration. All media contained 1 μM $FeCl_3$ plus the indicated level of either desferal or rhodotorulic acid (Sigma). The induction of iron stress was monitored using F_v/F_m measurements of photosynthetic efficiency (for diatom and flagellate) cultures or chlorophyll/ zeaxanthin levels for the cyanobacterium. Cell densities were monitored at intervals of 6 to 8 h with a Neurembauer hemocytometer and regression analysis of the experimental growth phase was used to calculate the growth rates.

Iron uptake rates were performed using 72 h old cultures, spiked with 2 nM $^{59}FeCl_3$. Cells were allowed to accumulate the radiotracer and sub-fractions harvested at 2, 4, 6 and 24 h. Titanium chloride-EDTA was used to remove unincorporated isotopes. Rates of iron accumulation were calculated using the linear portion of isotope burden versus time.

Field-based sampling

Sampling sites were located off the shelf break on a transect between the Galapagos Islands and the western coast of Peru. All sample water was collected by pumping from surface waters using an all plastic, trace metal clean system. Water for the bioassay experiments was drawn from nutrient-replete waters having comparatively moderate-to-low iron concentrations. Seawater was pumped through the system for several hours to rinse the tubing and pump assembly before collecting a homogenized surface (5 m) sample in a 50 L acid-cleaned polyethylene carboy.

The homogenized surface sample without filtration was distributed into 1000 mL polycarbonate bottles and specific quantities of artificial ligand (Desferal (DFB) or rhodotorulic acid (RA)) or iron (as $FeCl_3$). Triplicate bottles were prepared for daily sampling. Amended cultures were immediately placed in an on-deck, flowing seawater incubator. At the appropriate intervals, bottles were cleanly sampled for nutrients, viruses, bacteria and phytoplankton. Phytoplankton communities were analyzed immediately, without initial preservation, using a Becton Dickinson FACSCalibur flow cytometer equipped with a low argon laser and CellQuest software. In order to normalize the spectrum of cell responses, the software was calibrated using the following: 1, 2, 4, 10, 16 μm non-fluorescent beads for cell size based calibration and 10 μm fluorescent beads to standardized fluorescence corresponding to chlorophyll and phycocyanin.

Results

The yield and growth rate of each of the cultures was influenced by the total amount of iron in the medium (Fig. 1). The yield of all the cultures, except the diatom, were maximal when total iron added was greater than 10^{-6} M, but higher concentrations were required to achieve maximum yield in the diatom culture. As iron levels in the medium were reduced, the yield of the two flagellate cultures dropped quickly with little accumulated biomass when iron levels were less than 10^{-7} M. These flagellates did show an initial but unsustainable growth rate at these low iron levels, indicating that the low level of yield was a function of satiating the iron requirement of the cells, and not an issue of diffusion limitation.

The cyanobacterium and the diatom cultures contrast the growth kinetics of the two flagellates. In the case of the cyanobacterium, there was a rapid loss of cell yield and growth rate with a reduction of iron in the medium. The diatom culture remained active in growth and in the acquisition of iron throughout the different levels of iron, indicating that either more "available" iron was available for this cell or that the quota of this cell was considerably more "plastic" than the other cultures and the cell could maintain a growth rate at low iron concentrations.

If DFB was added to artificially reduce the level of "available" iron in the culture, the cells behaved differently than if the inorganic iron alone was reduced (Fig. 2). The flagellate strains had a more effective ability to remove iron from the complex than the cyanobacterium, whereas the diatom obtained sufficient iron for growth over the entire chelation range, even though the rate of iron transport was dramatically reduced (Fig. 3).

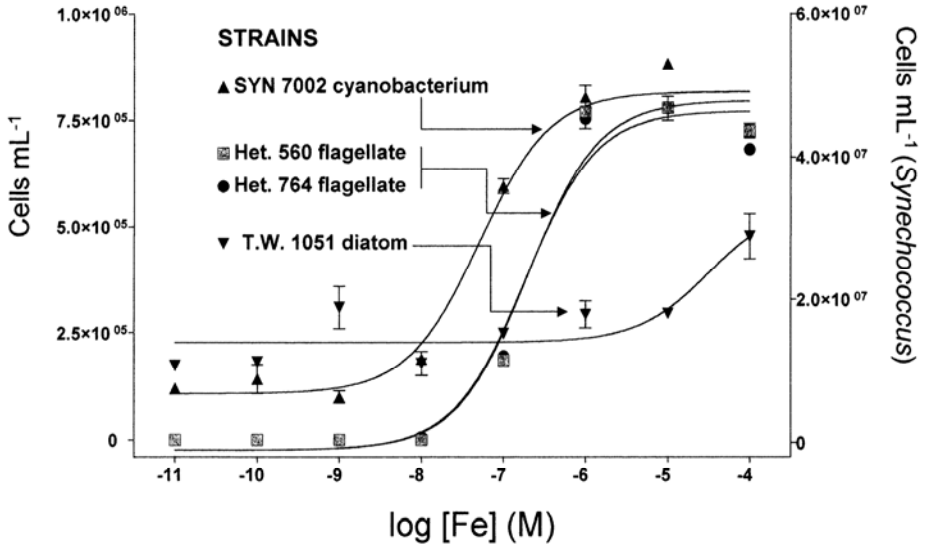

Fig. 1 The yield of the four phytoplankton cultures grown in media with different levels of total iron added.

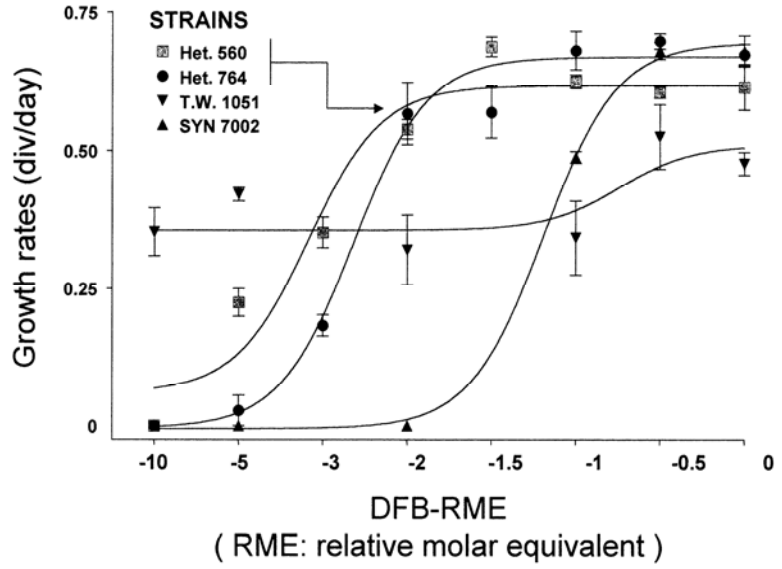

Fig. 2 The maximum growth rate of the laboratory cultures inoculated into media containing 1 µM Fe and the indicated level of DFB (Desferal). Growth rates are the maximum rates observed over a 10-day sampling period.

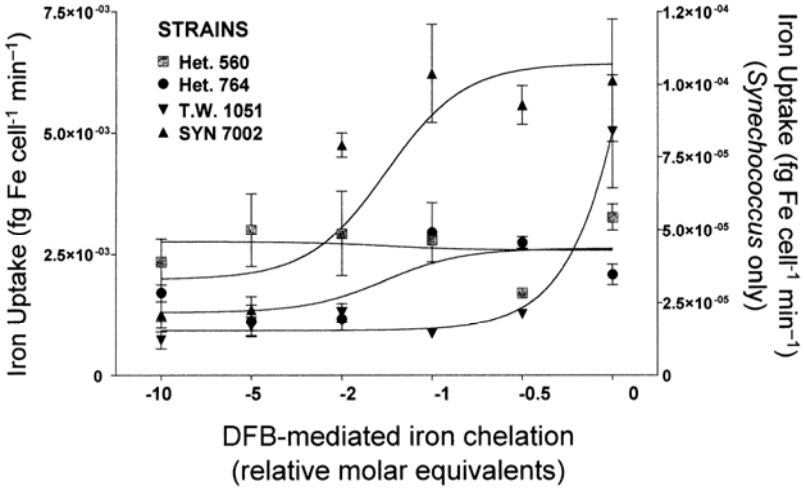

Fig. 3 The rates of iron accumulation mediated by DBF when the cells are exposed to an increasing level of xenosiderophore in the laboratory flask. Iron adsorbed to the cells was removed using the Ti-citrate wash.

Contrasting the addition of DFB to chelate the available iron, the addition of RA was stimulatory to the cyanobacterium and the diatom, while being as limiting to the two flagellates as the addition of the DFB (Fig. 4).

The addition of DFB to the natural population from the HNLC region southeast of the Galapagos Islands almost completely reduced the ability of the population to transform the available nutrients in the water mass. The water contained ~12 nM nitrate, ~9 nM silicate, and ~1.5 nM of phosphate. With the addition of iron to the sample, the final yield of the grow-out experiments was stimulated proportional to the amount of iron added. This stimulation only lasted for 3 days as the system was modified by grazers after Day 3 (Fig. 5).

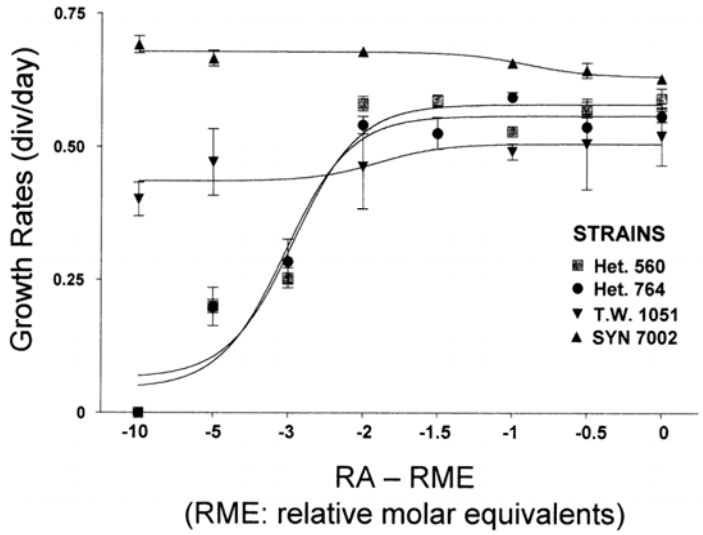

Fig. 4 The growth rates of the four laboratory cultures when the medium contained 1 μM $FeCl_3$ and the level of rhodotorulic acid (RA) was added. The *x*-axis is calculated based on a 2:3 ligand:iron binding ratio for RA.

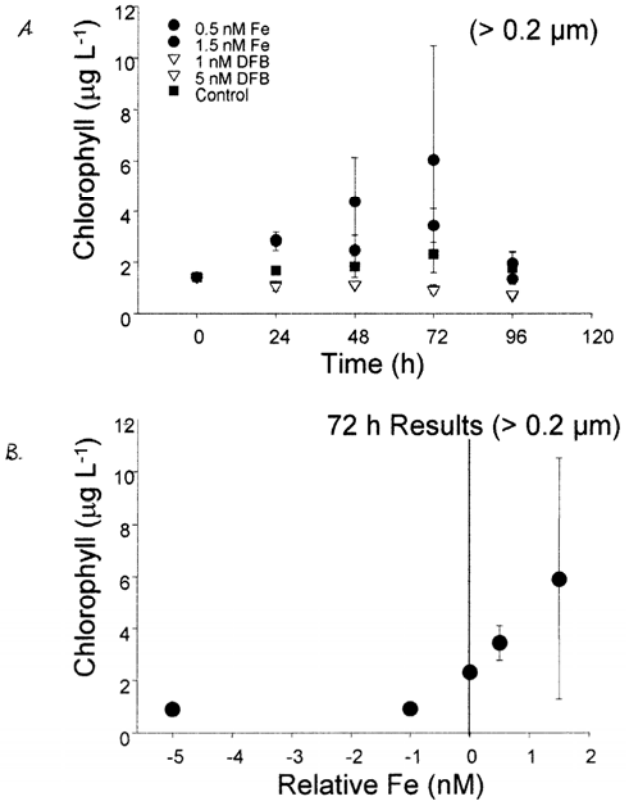

Fig. 5 The growth response of the natural population to the addition of (A) iron (as $FeC1_3$) and (B) DFB to chelate any other iron in the environment. The value of "0" indicated the non-supplemented waters.

The yield was proportional to the level of available iron in the system (Fig. 5B) but not all cells responded identically to the addition or removal of iron (Fig. 6). Figure 7 illustrates the response of four different types of photosynthetic organisms in the grow-out bioassays. In general, all the cells grew in response to the level of predictable iron, with the dramatic exception of the nanoeukaryotic cells (5–20 μm cells). These cells could compete for the available nutrients at low concentrations as the other cells were suitably inhibited by the lack of available iron. The nanoflagellates were growing in the low-iron waters in spite of having a dramatic reduction in the amount of chlorophyll per cell (Fig. 8).

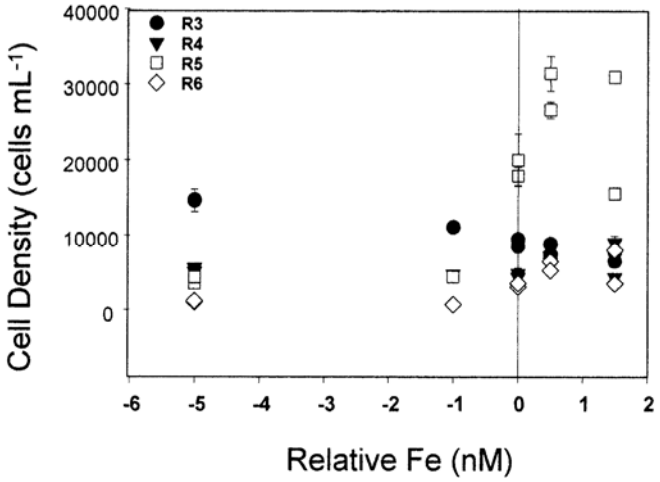

Fig. 6 The different responses of the community to the addition of either iron or the xenosiderophore. R5 is a PC-rich cyanobacterum. R6 is a PE-rich cyanobacterium. R3 is the response of the nanoflagellates in the system.

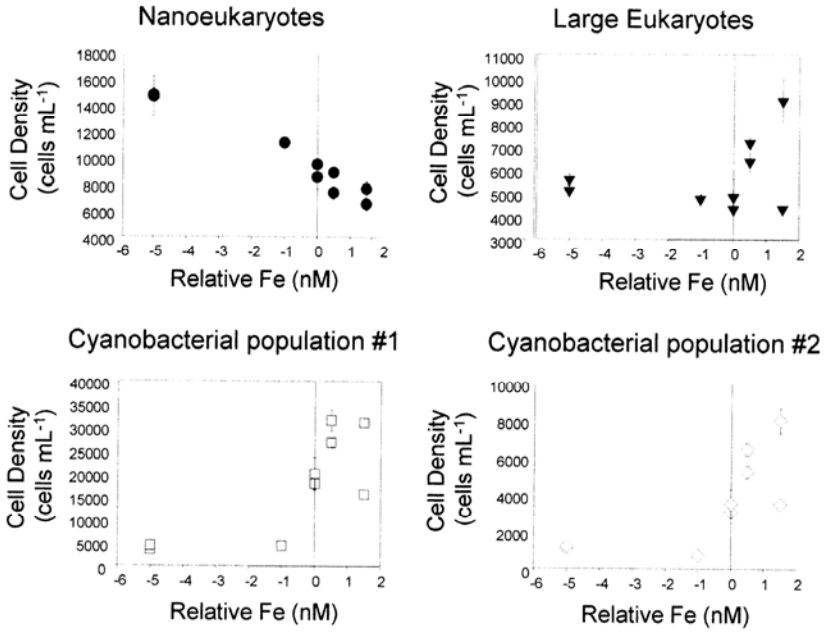

Fig. 7 A detailed look at the different cell populations in response to added iron or chelator.

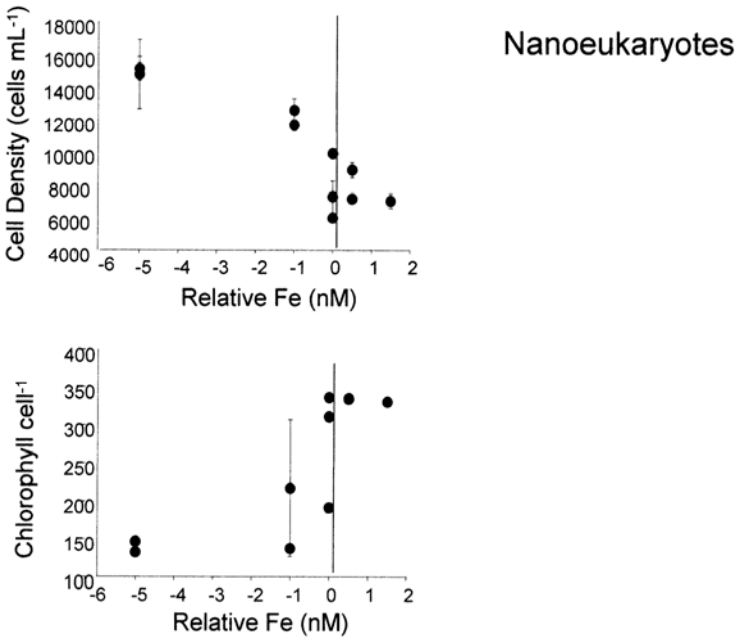

Fig. 8 The response of the nanoeukaryote community to the level of available iron. Even though the population continues to grow when iron levels are low, the lower panel indicates the level of chlorophyll within each surviving cell is dramatically reduced.

Discussion and conclusions

The importance of siderophores in cyanobacteria and the lack of extracellular "siderophores" from diatoms have created an artificial and unwelcome view of how iron is shared among members of the photosynthetic community. There are several points to bring forward:

1. Cyanobacteria are excellent producers of siderophores, and these may be the source of the natural ligand. But in non-marine systems, eukaryotes such as fungi, yeasts, and protests (photosynthetic and non-photosynthetic) are all active producers of iron-binding ligands (some of which have the low-iron inducible ligand–iron transport system and are thus "siderophores"; others are iron-binding "ligands"). Production of natural ligands by eukaryotic microorganisms remains under-appreciated.
2. Production of ligands from heterotrophic bacteria remains a possibility. While recent papers have indicated that carbon limitation remains the primary controlling factor even in HNLC regions, work by Price and by Cochlan (later in the workshop) should provide a new insight.
3. Field and laboratory observations indicate that cyanobacteria perform somewhat better than the larger eukaryotes when the xenosiderophore concentration is only in slight excess to the available iron. The growth of larger eukaryotes is very sensitive to the availability of the free iron in the system and there is no indication that any ability to obtain iron from the xenosiderophore–iron complex results in a competitive advantage of the cells.
4. The group that fills the void when the free iron levels drop and the ligand concentration increases over the natural levels of iron is the "nanoeukaryotes".

The reason for this dominance is not known at present but we could ask the simple question: Is it because they are "nano" or is it because they are mostly flagellates? We can pose several mechanisms. First, like many of the other photosynthetic protists, the photosynthetic system is reduced at higher ligand:iron concentrations. This is evident in chlorophyll/cell and parameters of photosynthetic efficacy. Since many of the observed cells are flagellates without predominant coccoliths (*Phaeocystis*, small dinoflagellates, *etc.*), iron acquisition through phagotrophy is a

possibility, thus circumventing the FIT/LIT model for the origin of available iron. Alternatively, there have been reports to suggest that the adsorption of small colloids to the complex surface of some flagellates will allow for a semi-portable iron pool, accessed through membrane-based reduction physiologies. If we can use our understanding from studies on coastal flagellates as examples, we conclude that the flagellates may have a higher level of adsorbed iron to the cell surface and a means to solubilize and utilize this iron pool.

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In situ testing of iron limitation in the Southern Ocean: An overview of the Southern Ocean Iron Enrichment Experiment (SOIREE)

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Introduction

The HNLC (high nutrient, low chlorophyll) regions account for approximately 30% of the ocean, of which the Southern Ocean occupies the largest surface area and represents the largest repository of excess nutrients. The role of iron as a limiting micronutrient of phytoplankton growth was suggested as early as the 1930s (see de Baar, 1994). Dissolved iron levels at sub-nanomolar concentrations and increases in phytoplankton biomass in response to iron addition have been confirmed for Southern Ocean waters (Martin *et al*., 1990a,b), and circumstantial evidence of iron-limited phytoplankton growth has been obtained in the Polar Front (PF) region (de Baar *et al.*, 1995). However, extrapolation from *in vivo* experiments is limited, due to the exclusion of grazing and physical controls (Banse, 1991), and causality in observational studies is difficult to prove. An alternative approach to establishing the relationship between iron supply and phytoplankton growth was achieved by mesoscale iron enrichment of surface waters in the equatorial Pacific (IronEx I), with tracking of the fertilised waters using a conservative tracer, sulphur hexafluoride (Martin *et al*., 1994; Law *et al*., 1998). A second study, IronEx II, unequivocally confirmed iron limitation in this region, with increased iron availability stimulating phytoplankton growth biomass and production despite increased grazing (Coale *et al*., 1996). Macronutrient concentrations declined in association with a drawdown of surface pCO_2 as inorganic carbon was fixed by the phytoplankton (Cooper *et al*., 1996).

These observations lent support to the "iron hypothesis" (Martin, 1990) that iron-mediated increases in export production may influence atmospheric CO_2. Yet, despite the 90-µatm decrease in surface CO_2 during IronEx II, the equatorial Pacific is not considered an important region for iron-mediated carbon sequestration, due to its limited capacity for transfer of fixed carbon into the deep ocean (Sarmiento and Orr, 1991). Instead, the Southern Ocean is considered to have the greatest potential to influence the oceanic CO_2 sink, due to the significant deep-water formation in this region. Indeed, 3-D ocean models predict that whatever limits nutrient uptake in the Southern Ocean constrains global atmospheric CO_2 on timescales of hundreds of years, with complete nutrient utilisation potentially resulting in a 6–21% decline in atmospheric CO_2 (Sarmiento and Orr, 1991).

However, the results of IronEx II cannot be extrapolated to the Southern Ocean, as factors such as light limitation (Sunda and Huntsman, 1997), co-limitation of diatoms by silicate availability (Boyd *et al*., 1999), and reduced physiological growth rates at lower temperatures may complicate the response to increased iron availability. Similarly, the response of biogeochemical cycling in the surface mixed layer to iron enrichment cannot be extrapolated from *in vivo* studies. Modelling simulations (Sarmiento and Orr, 1991) predict that iron enrichment would result in the complete utilisation of surface ocean macronutrients, yet significant variation has been observed in *in vitro* iron enrichments (de Baar and Boyd, 1999) and the open Southern Ocean (Comiso *et al*., 1993; Moore *et al*., 1999). The results of IronEx II confirmed the requirement for an *in situ* iron fertilisation experiment in open Southern Ocean waters to address the controls of the magnitude of phytoplankton stocks and the implications for atmospheric CO_2. The following discussion describes the results of the **S**outhern **O**cean **IR**on **E**nrichment **E**xperiment (SOIREE) which took place in February 1999 in the Austalasian sector of the Southern Ocean.

Methods

Site selection

Executing an *in situ* experiment, with the requirement to create and track a coherent body of surface water over a 2-week period was logistically and scientifically challenging in the dynamic environment of the Southern Ocean. Site selection for the experiment was critical to the success of the experiment and subsequent extrapolation of the dataset, and so site criteria were identified. The site had to be representative of a broad region of circumpolar HNLC waters, but with low current shear to maximise the timescale of patch tracking. The depth of the surface mixed layer had been regionally representative (see Fig. 1), but shallow enough to avoid iron/light co-limitation (Sunda and Huntsman, 1997), or over-dilution of the iron/SF_6. The pre-cruise desktop survey of bathymetry, sea surface temperature, mean mixed layer depth, wind speed, buoy drift trajectories from climatological datasets of WOA (World Ocean Atlas), JGOFS (Joint Global Ocean Flux Study) and satellite data, is described in Trull *et al.* (2001). Two regions were initially identified (Fig. 1), with 61°S 141°E chosen as the favoured site, partly because it was bounded by two major survey transect lines — R/V *Astrolab* and WOCE SR3 — which provided information on the major features in this region. The site was considered to be dynamically more stable due to a widening between the Polar Front and the southern Antarctic Circumpolar Current. The primary concern relating to the position of the site was the de-coupling of the silicate front from the Polar Front with the southerly migration of the former during summer. Bottle experiments in HNLC regions, IronEx II and observations from the Polar Front all suggest that diatoms were most likely to respond to iron addition, and silicate availability was therefore an important consideration. A 72-h pre-survey of the region confirmed that conditions were representative of polar open waters in summer (Table 1), and stable enough to initiate and maintain an iron-fertilised patch.

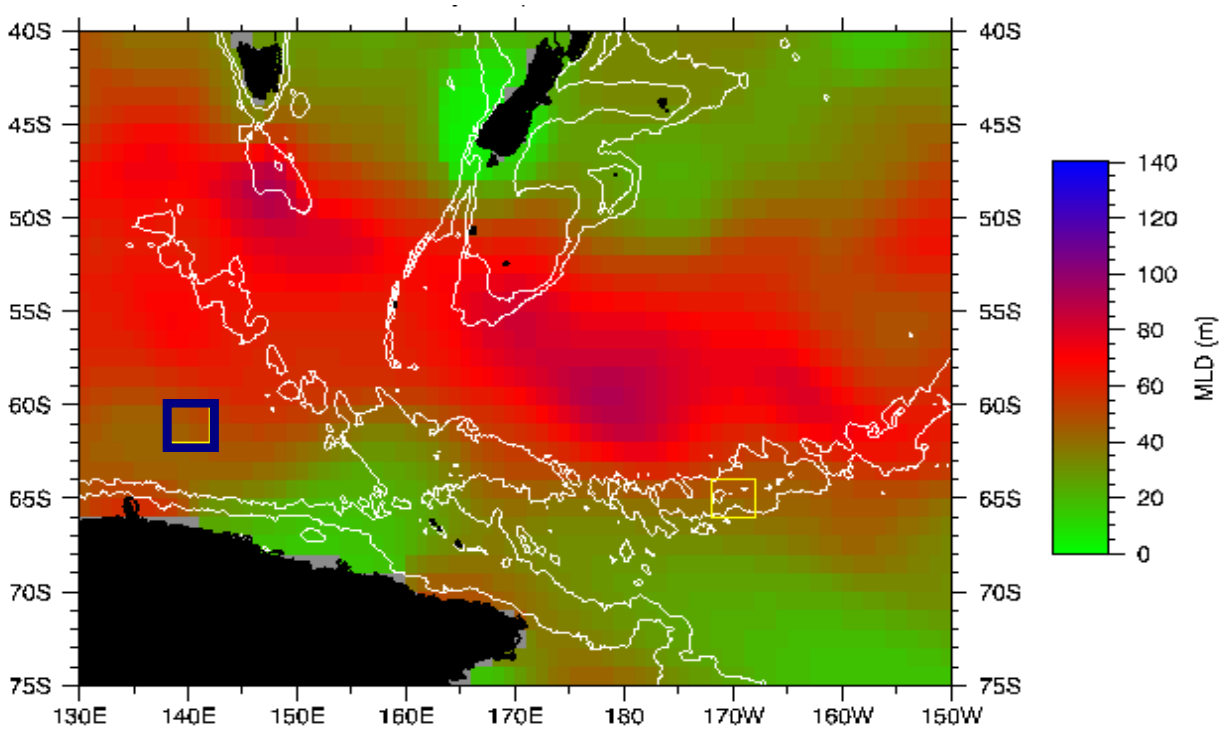

Fig. 1 The SOIREE site (blue box) at 61°S 141°E on a composite image of average mixed layer depth in summer (World Ocean Atlas).

Release

The release of 3.8 tonnes of acidified $FeSO_4$ and 164 g of tracer SF_6 took place on February 9, 1999 over approximately 50 km^2. The release was achieved by an expanding hexagonal track in a Lagrangian frame of reference around a central drifter buoy which updated its position every 10 min, allowing correction for surface water advection. Subsequent iron additions were initiated in response to low dissolved iron levels in the surface waters of the patch. The three subsequent infusions of iron on Days 3, 5 and 7 at the tracer patch centre were smaller (~1.6–1.8 tonnes) than the initial release and were not accompanied by SF_6, as the tracer signal remained high and the patch clearly defined throughout the experiment.

Methodologies are briefly described in Boyd *et al.* (2000) and in detail in the associated references for the following measurements: SF_6 (Law *et al.*, 1998); iron (Bowie *et al.*, 2001); Chlorophyll/ Production (Gall *et al.*, 2001b); DMS/DMSP (Turner *et al.*, 2004); CO_2/DIC (Watson *et al.*, 2000; Bakker *et al.*, 2001).

Table 1 Pre-infusion conditions at the SOIREE site (from Boyd *et al.*, 2001).

Property	
Temperature (C)	2.0±0.05
Density (kg m^{-3})	27.0±0.05
Mixed layer depth (m)	65.0±2.0
Chlorophyll *a* (μg L^{-1})	0.25±0.03
Nitrate (μM)	25.0±1
Silicate (μM)	10±0.4
Phosphate (μM)	1.5±0.2
Dissolved iron (nM)	0.08±0.03
Iron-binding ligands (nM)*	3.8±0.4
Algal community structure	Picophytoplankton-dominated
F_v/F_m	0.22±0.02
Diatom iron stress – (flavodoxin)	High
Euphotic zone depth (m, 1%Io)	84
Community primary production (0–65 m, mg C m^{-2} d^{-1})	150±17
Mesozooplankton stocks (0–70 m, g C m^{-2})	1.6 ± 0.86
Heterotrophic bacterial abundance (× 10^8 cells L^{-1})	3 ± 0.1

Results and discussion

Tracer and iron distribution

The patch drifted approximately 80 km east-southeast during the 13-day experiment and increased in surface area to 200–250 km^2. The tracer patch remained coherent throughout with the cross-patch width remaining constant at ~4–5 km and the along-patch length extending along its transit axis to ~30 km. The coherence of the patch enabled identification of the patch centre and borders and so ease positioning of the IN and OUT stations for vertical hydrocasts. The vertical structure of the patch did not vary significantly although transient structure developed within the 65-m surface mixed layer in the latter part of the experiment in response to improved meteorological conditions.

Iron was measured underway in surface waters and on vertical hydrocasts as dissolved iron (DFe – Fe(II) and Fe(III) that passed through a 0.2-μm filter) and total dissolvable iron (TFe) (Bowie *et al.*, 2001). The mean DFe during the initial mapping was 2.8 nM, close to the predicted release concentration, and observed concentrations in the Polar Front region (de Baar *et al.*, 1994). DFe fell

to 0.3 nM within 2 days to background pre-infusion levels (0.2 nM) due to rapid oxidation to Fe(III) to oxyhydroxides and soft colloids with subsequent aggregation. A similar trend was observed with the re-infusions, with DFe declining towards background levels, although TFe loss decreased prior to the final re-infusion on Day 7. After elevation to 2 nM on Day 7, DFe did not subsequently fall below 0.8 nM for the last 5 days of the experiment. The persistence of the elevated DFe was surprising and it appears that slower precipitation of the insoluble Fe(III) in the colder water of the Southern Ocean, combined with increased potential for photoreduction of Fe(III) to Fe(II), contributed. Furthermore, ~80% of the iron was in the reduced Fe(II) phase at the end of the experiment. This may have been associated with a doubling in the concentration of the Fe(III) ligands which was observed after the final re-infusion (Boyd *et al*., 2000; Croot *et al.*, 2001), leading to an increase in iron complexation capacity. The results indicate that biological mechanisms maintained iron availability in the surface waters of the Southern Ocean, leading to the persistence of the bloom.

Biological response

The response to increased iron availability was significantly slower than in the IronEx studies. This was expected due to the lower physiological rates at lower temperatures and lower light availability in the deeper surface mixed layer. The first biological response was recorded on Day 4 with an increase in F_v/F_m (see Fig. 2), a measure of the quantum efficiency of photosystem II and indicator of the general health of the phytoplankton (Boyd and Abraham, 2001). From Day 4, there was a steady increase in surface F_v/F_m during SOIREE, with an increase to the theoretical maximum of 0.65 in the lower surface mixed layer. Unlike IronEx II, there was no decrease in F_v/F_m after the last iron infusion.

This was followed by other physiological indictors, including decreases in iron stress (decreased flavodoxin expression) and decreased sinking rates (Boyd *et al*., 2000). There was a 5-fold increase in Chlorophyll *a* (Chl-*a*), from 0.4 mg/m^3 to 2 mg/m^3 by 13 days (Gall *et al*., 2001a,b), with an associated increase in column-integrated primary production from 0.2 g/m^2/d to 1.5 g/m^2/d. This exceeded the increase in biomass observed during IronEx I, but was less than the 30-fold increase during the Ironex II study (Coale *et al*., 1996). The elevated Chl-*a* concentrations observed were of similar magnitude to that associated with elevated iron concentrations in the Polar Front region (de Baar *et al*., 1995). C:chlorophyll ratios decreased from 90, prior to the experiment, to ~45 by Day 13, with phytoplankton carbon increasing by 3-fold. Silicate utilisation in the presence of iron was more efficient, with Si:C uptake ratios decreasing from 0.17 in surrounding waters to 0.09 in the iron-enriched patch (Watson *et al*., 2000).

The increase in chlorophyll was interpreted as an increase in chlorophyll per cell in the smaller size classes followed by floristic shifts with an increase in the number of large cells. Size fractionation of the Chl-*a* confirms that the smaller groups responded first, possibly reflecting their capacity to sequester iron faster (Gall *et al*., 2001a). However, by Day 8 the smallest size fraction, <2 µm, crashed in response to an increase in zooplankton grazing (Hall and Safi, 2001). The 5- to 20-µm size class was dominated by the flagellates and increased around Day 7–8 and plateaued towards the end of the experiment. The largest size class, consisting primarily of diatoms, dominated and accounted for 75% of primary production during the experiment. The diatoms were predominately *Fragilariopsis kerguelensis*, a common Southern Ocean bloom-forming species with a high silicate requirement. The increase observed in all size classes indicates that community structure was determined by iron availability, with dominance by the larger diatoms confirming previous observations.

Biogeochemical response

Macronutrient concentration did not exhibit a decrease until Day 5, with nitrate, phosphate and silicate decreasing by 3, 0.22 and 2.5 µM, respectively, by Day 13 (Boyd *et al*., 2000). As in IronEx II, inorganic carbon uptake was significant with CO_2 drawdown in the surface waters of the iron/tracer patch. Continuous measurement of the surface fCO_2 signal patch indicated a clear divergence between the iron-fertilised patch and surrounding waters with a small temperature-related increase in fCO_2 outside the patch and a decrease of ~30 µatm inside (Watson *et al*.,

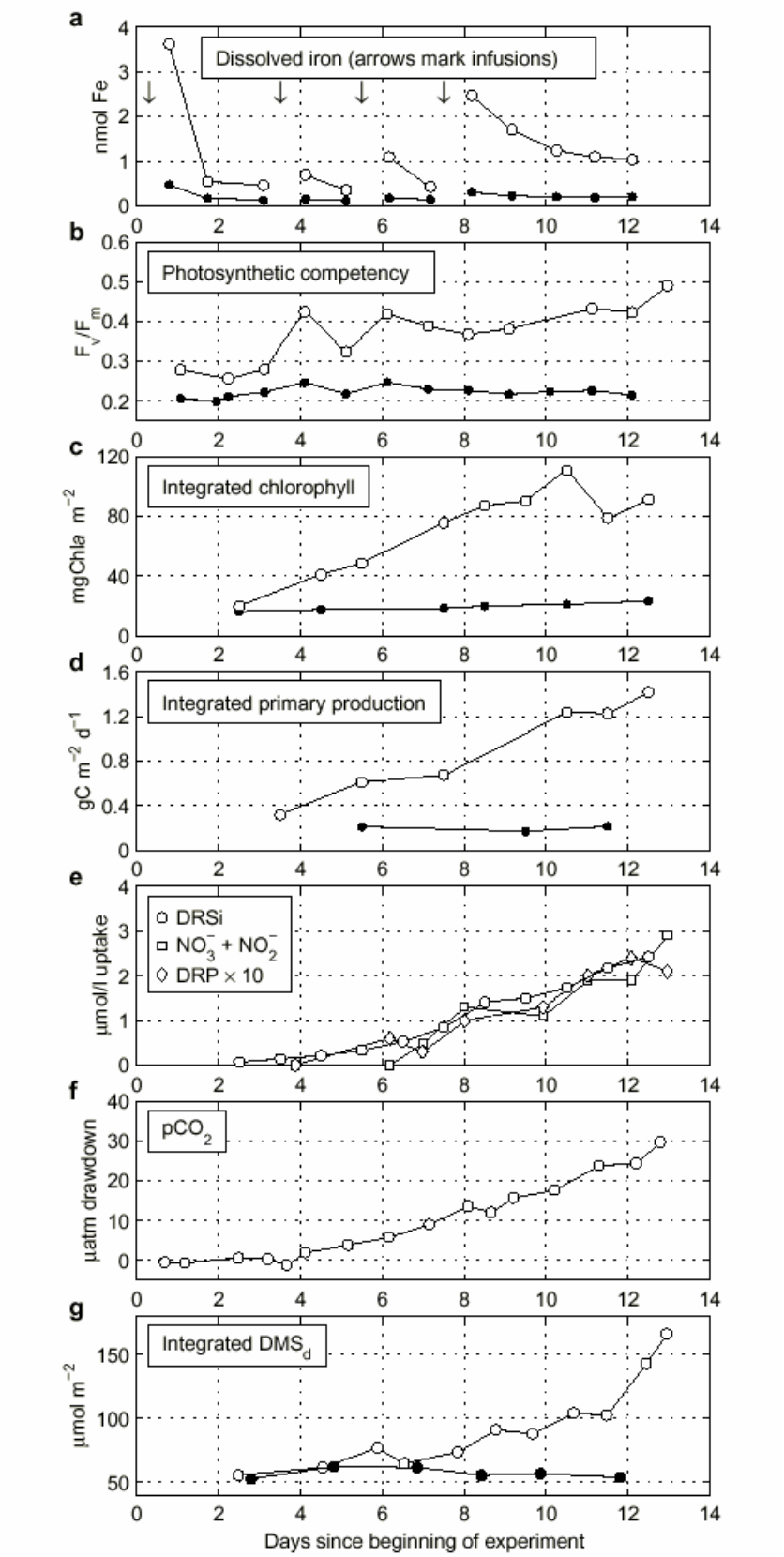

Fig. 2 Biological and biogeochemical response to iron fertilisation during SOIREE (Boyd *et al*., 2000).

2000; see Fig. 3). The drawdown of CO_2 was similar in magnitude to that associated with elevated iron in the Polar Front (de Baar, 1994). DIC decreased by ~15–18 µmol/kg, consistent with the fCO_2 and nitrate drawdown (Bakker *et al.*, 2001).

The increase in phytoplankton production and a shift in community structure stimulated dimethyl suphide (DMS) production during IronEx II (Turner *et al.*, 1996). DMS accounts for a significant proportion of the biogenic sulphur flux to the atmosphere, particularly in remote regions such as the Southern Ocean where it is oxidised to sulphate aerosols, and subsequently influences reflectance and cloud albedo (Charlson *et al.*, 1987). DMS derives from the precursor dimethyl-sulfionproprionate (DMSP) which is an intracellular osmolyte used by certain species of phytoplankton. During SOIREE, particulate DMSP increased to Day 8–9, and then declined, mirroring the 5- to 20-µm phytoplankton size fraction, and suggesting that the primary source of DMSP was the flagellates. DMS levels increased from Day 7, coincident with increased herbivory by the microzooplankton, and were still increasing on Day 13. It is speculative as to whether the DMS would have continued to increase, as diatoms are not generally regarded as significant sources of DMSP. The DMS increase observed during SOIREE was greater than that of IronEx II (7-fold compared with 3-fold compared with initial DMS concentrations, Turner *et al.*, 2004). The SOIREE results support the contention that an increase in iron flux to the Southern Ocean could stimulate DMS flux and impact atmospheric albedo in this region.

The results indicated potential for enhanced export into the deep ocean, with an increase in the biological pump. However, the phytoplankton were relatively healthy on departure (Boyd *et al.*, 2000), and the mesozooplankton response to the increased phytoplankton biomass was limited (Zeldis, 2001). The latter may be attributable to the heavily silicified *F. kergulensis*. Thorium-234 measurements, particulate organic carbon, and biogenic silicate collection in free-drifting sediment traps at 100 m all suggested that no significant export occurred during the 13-day experiment (Charette and Buessler, 2000; Nodder *et al.*, 2001). The accumulation of algal carbon (~4.1 g C/m^2) accounted for ~70% of iron-mediated algal C fixation (6.1 g C/m^2). However, there was evidence of increasing iron stress, aggregation and sinking rates towards the end of the experiment (Boyd *et al.*, 2000).

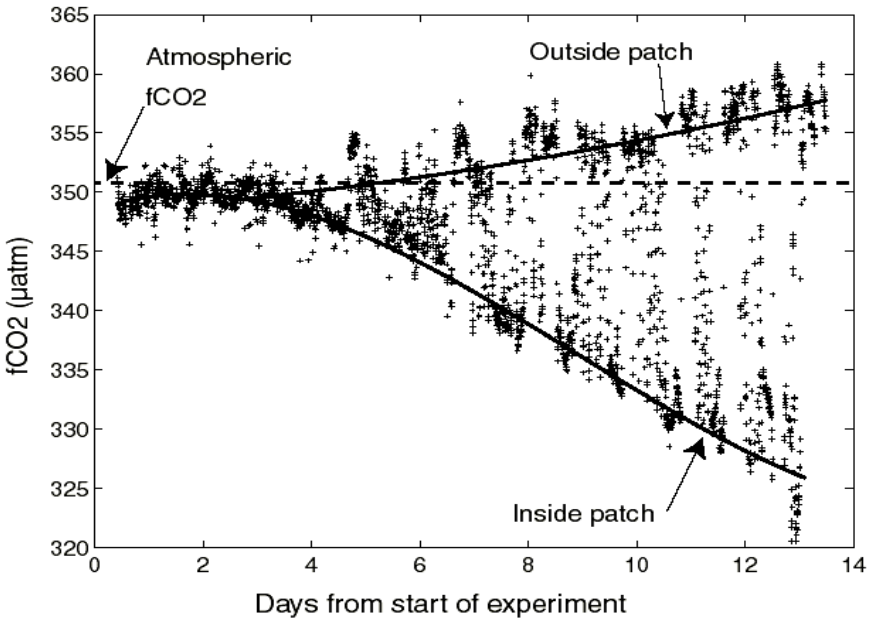

Fig. 3 Response of surface fCO_2 to iron fertilisation during SOIREE (Watson *et al.*, 2000)

Bakker *et al.* (2001) estimate that an additional 1350 tonnes of carbon would be transported into ocean interior on subduction, although Trull *et al.* (2001) suggest that subduction in this region would be unlikely. The persistence of the bloom, as evidenced by elevated Chl-*a* levels in satellite images of the region, confirm that subduction did not occur, and suggests that export was not significant for the 6- to 7-week period following SOIREE (Abraham *et al*., 2000). An elliptical feature of length ~150 km and surface area ~100 km^2 was observed with Chl-*a* levels exceeding 3 mg/m^3, which exceeds the maximum concentrations recorded for this region. Evolution of the bloom into a filament indicates that stirring not only controlled the dispersion but also the development of phytoplankton blooms. Analysis indicates that the patch was spreading at a low enough rate for phytoplankton growth to accumulate biomass and for the iron to remain above a critical level, but high enough to maintain silicate entrainment for diatom growth. Furthermore, the persistence of the bloom indicates that the majority of the iron that remained in the surface waters on Day 13 was still available 6 weeks later (Abraham *et al*., 2000).

Conclusions

SOIREE has successfully demonstrated that the significance of iron in water was broadly representative of 75% of polar waters during the austral summer in this region of the Southern Ocean. The results indicate that iron controls the magnitude of production and community composition, and further support the link between iron, phytoplankton and climate, although the ultimate fate of the iron-mediated bloom is speculative. The observations have raised fundamental questions relating to iron biogeochemistry and retention in the surface ocean, and identified the importance of stirring to the maintenance of phytoplankton blooms.

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A1.2.2 Chemistry in the North Pacific and IronEx

Iron distribution in the Northeast Pacific Ocean

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Introduction

This paper describes the preliminary results on the spatial description of iron in the Northeast Pacific Ocean, being conducted on board the CCGS *John P. Tully* for a joint project between the Climate Chemistry Laboratory of the Institute of Ocean Sciences (IOS, Canada) and the Biology Department of the Central Research Institute of the Electric Power Industry (CRIEPI, Japan).

The upper waters of the subarctic Pacific Ocean, equatorial Pacific and Southern Ocean are the three major HNLC (high nutrients, low chlorophyll) regimes in the world oceans. They are characterized by a shortage of iron as a micronutrient, thus inhibiting the growth of diatoms and limiting the full utilization of the macronutrients available in the surface mixed layer. The seasonal and spatial distributions of iron are therefore, fundamental to understanding the availability and utilization of this essential micronutrient by diatoms in HNLC waters.

Iron in seawater is difficult to measure due to the ubiquitous presence of iron as a contaminant in the sampling and measuring procedures, with dust in the air and rust from ship and oceanographic sampling gears and wires. Extreme care is required in all phases of shipboard sampling and analysis to ensure data integrity. This paper describes the salient points in the detection of iron in seawater, results of recent measurements from IOS cruises on Line P and Station P, and a project to study mesoscale eddies in the Northeast Pacific Ocean. Nishioka *et al*. (2001) describes the distribution of soluble and small colloidal iron for these cruises.

The definitions used to distinguish different forms of dissolved iron are: (1) labile, unfiltered seawater, (2) dissolved, <0.45µm, (3) labile particulate, (1) minus (2), (4) colloidal, between 0.1 and 0.45 µm, and (5) soluble plus small colloidal, <0.1 µm. In this study, the main form discussed here is labile (sometimes called total dissolvable) iron.

Methods

Samples for iron analyses were collected under two separate projects: (1) a Station P/Line P monitoring study and (2) an eddy study in the Northeast Pacific Ocean. For project (1), iron distribution on Line P from the west coast of Vancouver Island to Station P (*i.e.*, P26) is shown in Figure 1, with sampling stations at regular oceanographic stations of P04 (48º 29′N, 126º 40'W), P12 (48º 58′N, 130º 40′W), P16 (49º 17′N, 134º 40′W), P20 (49º 34′N, 138º 40′W) and P26 (50º 00′N, 145º 00′W). At these stations, hydro-casts for iron samples were made for depths of 10, 25, 75, 100, 200, 300, 400 and 600 m as well as 800 and 1000 m in more recent expeditions. Surface sampling was done from a Zodiac rubber boat. For the Eddy Project (project 2), iron sampling was made during special cruises to monitor the water properties at the edge and inside the eddy as it moved from the coastal ocean towards the vicinity of Station P. Similar profiles for iron were made, as described for the regular Station P/Line P monitoring project.

Sampling of seawater for the iron study was done in several ways. At hydro-stations, 30 Go-flow™ samplers were pre-cleaned in the laboratory by sequential soaking with 5% Extran for about 1 day, then 0.1% HCl or dilute 0.1M ascobic acid, or a mixture of both, for a few days with DMQ rinses in between. At sea the samplers were filled with seawater at low iron levels for about 1 day for soaking.

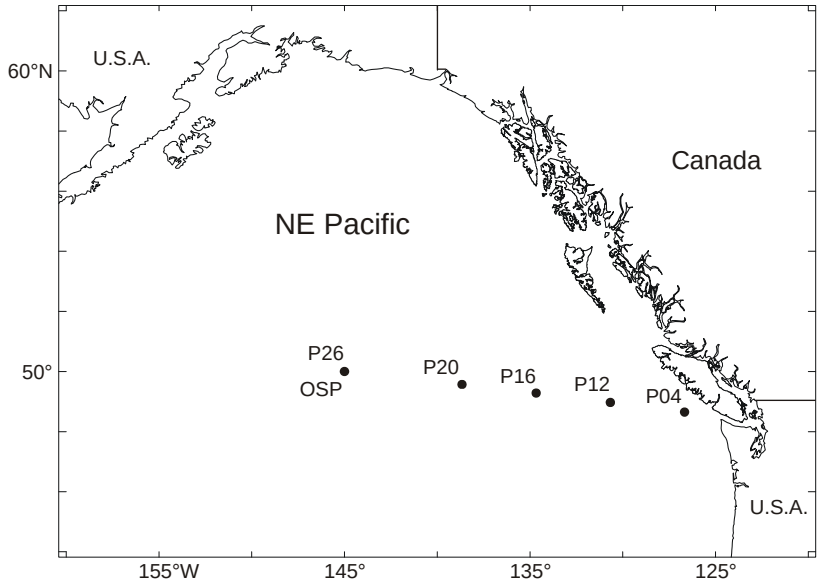

Fig. 1 Position of stations along Line P.

Samples from 75 m and below were collected using 30 L (or 10 L for Station P04 only) bottles on a 1,000-m Kevlar line spliced to the hydrowire on a hydro winch, with a layer of plastic separating the Kevlar from the steel line. Lead weights, freshly encased in epoxy resin, were attached to the end of the Kevlar line. Shallow samples at 10, 25 and 40 m were also collected using an air-driven Teflon pump and Teflon sampling tube with handling done in a PVC HEPA clean hood on deck. Seawater samples were drawn from Go-flow™ samplers on deck using boxes with extended sides and roof to minimize air disturbance. A Teflon tube was attached to a Teflon valve on the Go-flow™ and on the other end, a bell jar covered the sample bottles during sub-sampling. Two to six 250-ml pre-cleaned CPE bottles, after rinsing three times, were immediately filled with seawater. Normally, two were unfiltered, and one each was filtered through a 90 mm 0.45 µm Durapore membrane filter, and a 0.1µm (0.22 µm used since June, 2000) Opticap cartridge by Millipore.

Analysis

Iron analyses were made inside a shipboard clean laboratory of about 10′ × 7′, constructed with polyethylene sheets with a small entry cubicle. A positive-pressure clean hood (Class 100 EACI laminar flow work station at ~360 cubic feet per minute) with a Class 100 HEPA filter created a clean space for reagent preparation and sample processing. A tacky mat at the entrance eliminated dirt on shoes and personnel entering the clean room wore clean plastic suits with hoods, boots and gloves. A milli-Q ultra-violet system inside the clean room supplied high purity water (DMQ) for reagents, standards and cleaning.

A chemiluminescence technique (Obata *et al*., 1993) with modifications (Obata *et al*., 1997) was used. A semi-automated system, constructed by the Climate Chemistry Laboratory, was used. The method is a combination of selective column extraction using chelating resin and chemiluminescence detection. Samples were buffered to pH 3.2 using a buffer solution of formic acid-ammonium formate. Samples were delivered to the system using an eight port valve (Hamilton MVP 8) and a peristaltic pump. About 4–16 ml were passed through a resin column of 8-hydroxyl quinnolin immobilized on silica gel at a flow rate of 4 ml per minute. The iron was then removed from the column using dilute HCl (0.3N). The resulting eluent was then mixed with luminol, aqueous ammonia and hydrogen peroxide, prior to entering the cell (Teflon tubing coiled on a mirror). A Hamamatsu photo multiplier tube measured the light emitted from the chemiluminescent reaction of the iron and luminol as the eluent passed through the cell with the resulting signal recorded on a laptop computer.

Reagents

The reagents were prepared as described in Obata *et al*. (1997): Seastar ultrapure grade HCl and NH_4OH, re-crystallized luminol and TETA (triethylene tetramine), K_2CO_3 (Merck Suprapure grade), H_2O_2 (Baker Ultrapure grade) and twice quartz distilled HCOOH. The 8-quinolinol immobilized chlelating resin was obtained from Dr. H. Obata. Reagents were prepared in advance to allow for degassing of the aerated DMQ between the feed source on the ship and the shipboard laboratory.

Standards

AAS Standard Fe(III) of 1,000 ppm solution commercially available was used to prepare a primary standard (1,000 ppb) and secondary standard (10 ppb), which were used to prepare fresh daily working standards. Seawater, collected from Station P surface waters and filtered through a 0.1 μm cartridge filter, was used to make up standards. The iron content was < 0.l nM.

Results and discussion

The study area covered Line P (48.5ºN, 126ºW to 50ºN, 145ºW) and Line Z (47°N, 145°W to 59.5°N, 145°W). At Station P, inter-calibrations (Fig. 2) were made between IOS and CRIEPI using basically the same technique and sampling equipment. John Martin's profile (Martin and Fitzwater, 1988) in 1987, using the atomic absorption technique, is also plotted in the figure for comparison. There was good agreement between IOS and CRIEPI for seawater at a depth lower than about 400 m, while in the upper ocean the CRIEPI values were slightly higher.

The vertical profiles (0–1,000 m) of unfiltered labile (LFe) iron for June 1998 (cruise #9815) on Line P (Fig. 3), showed relatively low (<0.1 to 0.4 nM) iron in the surface 50 m. At coastal station P04, iron increased rapidly to a high value of 4.5 nM at 600 m, then decreased slowly to 3.6 nM at 1,000 m. Station P12 showed a slightly higher value in the upper 100 m and below 500 m compared to the other offshore stations. For the offshore stations P16, P20 and P26 (Station P) in the HNLC waters, iron values were generally < 0.1 nM in the upper 100 m with a small increase to about 0.5 to 0.6 nM at depths from 400 to 1,000 m.

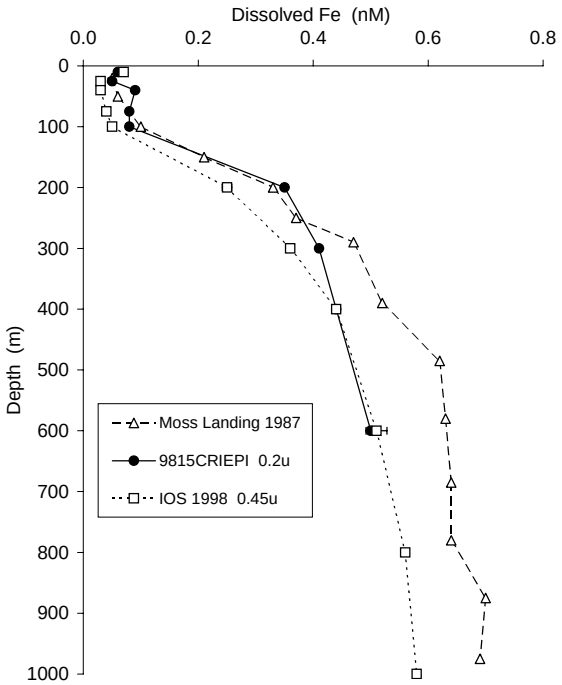

Fig. 2 Intercomparison of iron measurements done near Station P (P26) by IOS, CRIEPI and earlier, by Moss Landing Marine Laboratory (Martin and Fitzwater, 1988).

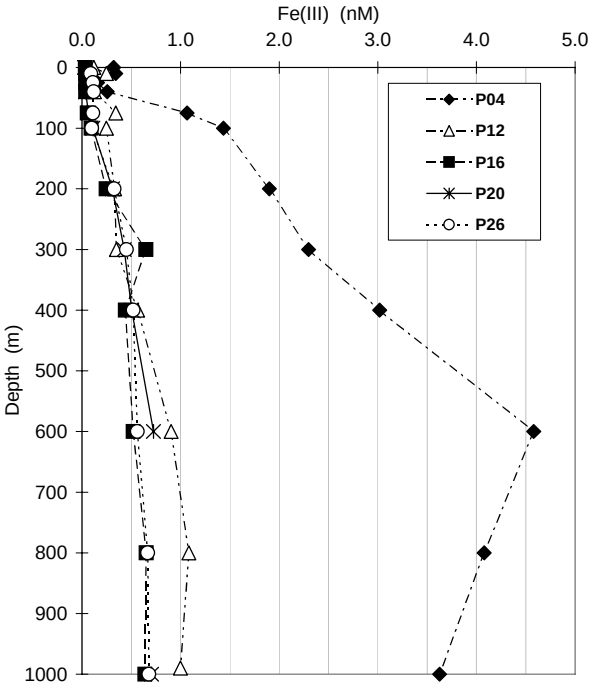

Fig. 3 Vertical distribution of unfiltered iron (Cruise 9815) at stations P04, P12, P16, P20 and P26 along Line P.

Horizontal surface iron distribution (labile and dissolved, 0.1 µm filtered) at depths of 10 and 20 m in September 1997 is shown in Figure. 4. There is a high coastal labile iron concentration at 0.75 nM and much lower distribution of <0.15 nM farther offshore from P19 to P26. At Station P17 (at 136°W), there is marked increase to 0.35 nM and for stations at 143°W and 145°W, a smaller increase to 0.2 nM, indicating possible transport of iron-rich waters either vertically or by eddies.

The Haida Eddy is a slow-moving eddy formed near the Queen Charlotte Islands, off the west coast of British Columbia. The eddy is anti-cyclonic, has a diameter of about 200–300 km, and moves at about 3–5 km per day to the west towards Station P. The Haida Eddy 1998, formed just outside Queen Charlotte Islands in February 1998, moved in a path opposite to the direction of the Alaskan arm of the eastern sub-arctic gyre, first southward along 134ºW to 48ºN 136ºW (February 1998), then southwestward towards 46ºN 141ºW (February, 2000). Iron measurements from the surface to a depth of 600 m were made at the centre, the edge and outside the eddy (Fig. 5) in Haida 2000. In the centre, labile iron in the surface mixed layer down to 50 m was about the same as at the edge of the eddy. To the south of the eddy, the labile iron was higher in the surface due to coastal seawater streaming from Hecate Strait.

Open ocean values are shown from P20 to demonstrate how much more iron is found in coastal and eddy seawater. Below the pycnocline at about 100–120 m, labile iron from the centre of the eddy was much higher than the values at the edge and outside the eddy. This indicated that the centre of the anti-cyclonic Haida Eddy conserved high iron after it left the coastal zone. The original depth of the Haida Eddy was thought to be 200 to 300 m, indicating that some iron was being transported to depth as the eddy aged. The iron content after filtration through a 0.22 µm Millipore/Durapore filter, was only 25% lower. The same is true for the stations at the centre and on the edge of the eddy. By September, the surface iron was probably approaching limits for the Haida Eddy when both labile and dissolved iron (<0.22 µm) in the whole upper 75 m were both below 0.05 nM while water below this was still more than double what was found at P20.

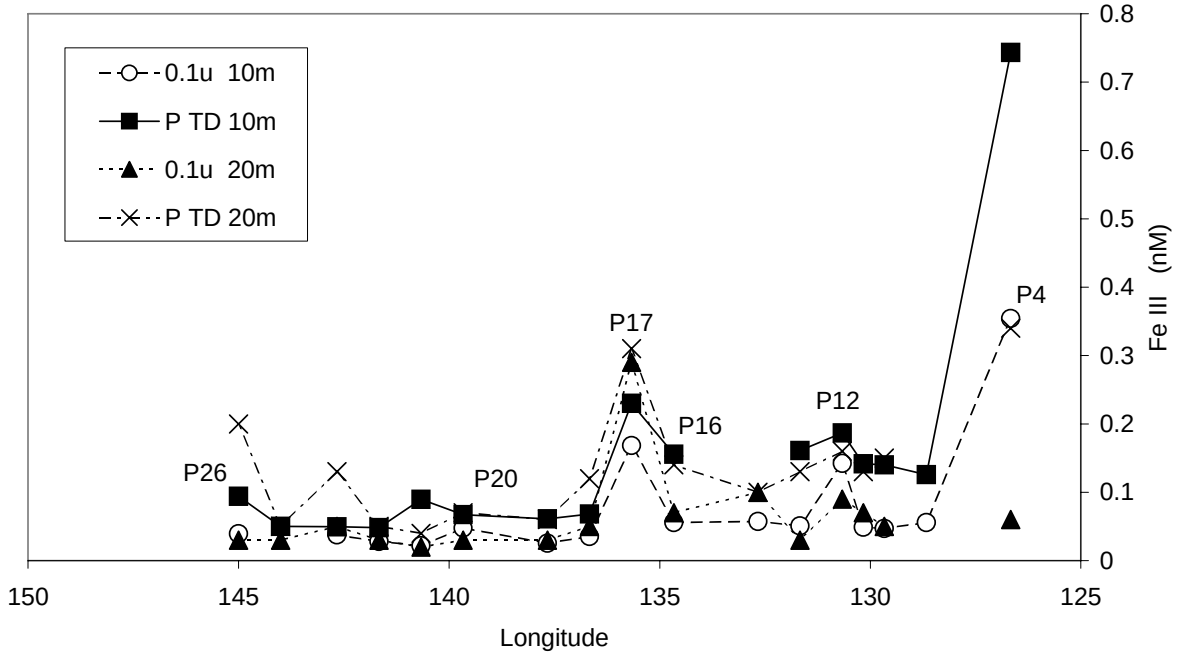

Fig. 4 Horizontal distribution of iron along Line P in September 1997.

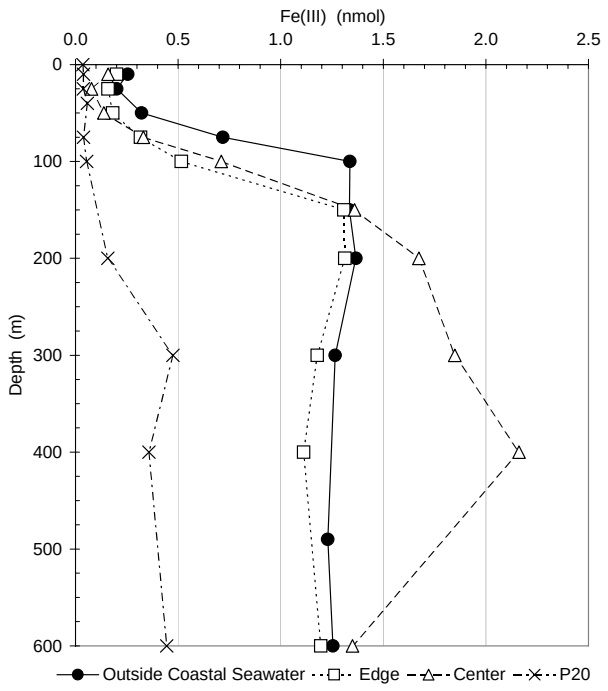

Fig. 5 Distribution of unfiltered buffered (labile) iron at the edge, inside and outside the Haida Eddy in June 2000.

Conclusions

1. Shipboard iron measurements by chemi-luminesence technique using clean reagents, sampling procedures and analytical environment are compatible between CRIEPI and IOS laboratories.

2. The vertical distribution of iron in HNLC waters in the Northeast Pacific showed very low surface values while in deep waters, iron was high but was prevented from reaching the surface mixed layer because of a strong pynocline at 100 m depth.

3. The horizontal distribution of iron in September, 1997, from coastal to open-ocean waters showed a progressive decrease, with high values of 0.8 nM just west of Vancouver Island to <0.1 nM at Station P (P26) with high values at Station P17 in between, suggesting the possibility of eddy transport of high iron from coastal waters to offshore.

4. In an eddy study in the Northeast Pacific to track the change in water properties, iron distribution was measured at the edge, outside and at the centre of the Haida Eddy. Coastal iron outside and at the edge of the eddy showed similar features with depth, but in the centre of the eddy below the pycnocline, iron was almost doubled, suggesting that iron was trapped inside the eddy. Compared with open ocean seawater, the eddy contained more than four times as much iron below 75 m.

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Iron and manganese distribution in the surface waters of the North Pacific Ocean and the Bering Sea

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The distributions of iron and manganese in the surface layers were investigated in the North Pacific Ocean and the Bering Sea. Samples were collected during the research cruise of R/V *Hakuho-maru* (University of Tokyo), KH-99-3 (from June 25 to July 22, 1999). Iron and manganese concentrations were determined with automated chemiluminescence methods (Nakayama *et al*., 1989; Obata *et al*., 1993, 1997). Iron was depleted at 0–50 m all through the sampling stations, but iron concentrations below 50 m showed contrasting distributions between the western and the eastern sides of the North Pacific Ocean, and the Bering Sea. To discuss the difference in the iron sources between the stations, iron distributions were compared with those of manganese. As the residence time of manganese in the surface layer is relatively long (5–19 yr, Landing and Bruland, 1987), manganese is suitable as a tracer for the supply of a lithogenic substance. The relationship between nitrate and silicate in the surface layers also showed various patterns in each oceanic regime. Iron limitation is reported to affect the uptake ratio of silicate to nitrate by diatoms (Takeda, 1998), and the supply of iron may influence the relationship between nitrate and silicate in the surface layer.

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Assessment of the lower limit of iron addition required to initiate massive diatom blooms in the eastern equatorial Pacific

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Introduction

The issue of iron limitation in the oceans has garnered rapidly increasing interest since the successful mesoscale iron enrichment experiment in the equatorial Pacific known as IronEx II. This experiment demonstrated unequivocally that iron is limiting diatom (and thus export) production in the eastern equatorial Pacific high nitrate, low chlorophyll (HNLC) regime (Coale *et al.*, 1996). Iron infusion transformed the oceanic picoplanktonic phytoplankton assemblage into a coastal-type pennate diatom-dominated assemblage, increasing total chlorophyll levels 20 times over levels outside the enriched patch. The accompanying macronutrient and TCO_2 depletion during the first 12 days of the bloom testify to the major geochemical impact that iron flux alone can have in this region (Steinberg *et al.*, 1998).

Although the IronEx II enrichment study clearly demonstrated iron limitation of phytoplankton production, the experiment was not designed to ascertain the minimum iron flux needed to generate large diatom blooms in equatorial Pacific waters. Iron concentrations generated within the infused patch (2 nM) were low by coastal standards but were massive in comparison to ambient levels, raising iron concentrations by two orders of magnitude. Assessing the lower limit of required iron enrichment is important because it provides insight to the scale of natural perturbations that could cause these types of bloom events. For example, if high iron flux is required, then significant iron-induced increases in export production could only be a response to climate change. However, if comparatively minor increases in iron flux are necessary, then increased export production might precede and contribute to global climate change.

Although there remains uncertainty about which iron species are available to phytoplankton in general, and diatoms in particular, iron uptake appears to be restricted to the truly soluble, or low molecular weight fraction in seawater (Wells *et al.*, 1995). Here, I present results from cross-flow filtration (CFF) studies during IronEx II where iron was partitioned into dissolved (< 0.4 µm), soluble (< 1 kDa) and colloidal (1 kDa to 0.4 µm) size fractions. The results demonstrate that the soluble iron fraction increased only minimally despite nanomolar iron additions, the bulk of added iron occurring in the colloidal size phase. Soluble iron concentrations changed in conjunction with chlorophyll increase and macronutrient drawdown. The relative drawdown of silicic acid and nitrate suggest the diatom population continued to experience iron stress throughout bloom development, despite calculations indicating the pennate diatoms were not diffusion limited at the concentrations of soluble iron measured. These findings help to constrain the magnitude of iron flux needed to initiate and sustain large phytoplankton blooms in equatorial HNLC waters.

Materials and methods

Samples were collected from various locations near the center of the enriched patch (marked by a drogue buoy) using Teflon®-lined 30 L GO-Flo bottles (General Oceanics) on a Kevlar line (Philadelphia Resins). M. Gordon (Moss Landing Marine Laboratory) kindly provided 20 L carboys of conventionally filtered (< 0.4 µm) samples for processing. These 20 L dissolved samples were then further size fractionated by CFF using a 1-kDa membrane (Filtron). Details of the steps used are given in Wells (2003). CFF processing was completed within ~ 5 h of sample collection. Samples were acidified with 4 ml of quartz-distilled 6 N HCl per liter and stored for several months before extraction and analysis.

The dissolved (< 0.4 µm), permeate (< 1 kDa) and retentate (1 kDa to 0.4 µm) samples were extracted before analysis using a new solid phase extraction procedure (Wells and Bruland, 1998). Sample

extracts were analyzed on a Finnigan MAT ELEMENT magnetic sector (high resolution) ICP-MS. Colloid concentrations were calculated using the concentration factor (*cf*) of the individual CFF run and the measured metal concentrations in the retentate and permeate fractions:

$$[colloid] = \frac{[retentate] - [permeate]}{cf}$$

This quantification of colloid concentrations is more robust than simply subtracting permeate (< 1 kDa) from total dissolved (< 0.2 μm) concentrations because: (1) the latter depends on accurately measuring the difference between two large numbers, and (2) the mass balance can be determined for each CFF run:

$$[< 0.2\mu m] = [permeate] + [colloid]$$

Good agreement between the sum of permeate and calculated colloid concentrations with dissolved values is strong evidence that CFF processing was not significantly influenced by contamination or sorptive losses of soluble or colloidal species to the membrane.

Results

Results from pre-release sampling indicate that ~85% of the ambient dissolved iron was soluble in nature, with ~3 pM Fe occurring in the colloidal phase. Reliable identification of such a small colloidal component within the dissolved phase would be impossible from the simple difference between dissolved (< 0.4 μm) and permeate (< 1 kDa) values. However, the comparatively high retentate concentration (152 ± 22 pM Fe), along with the good mass balance (104%), raises confidence that the extent of the soluble/colloidal partitioning is reasonably accurate.

Dissolved iron concentrations within the enriched patch cycled repeatedly from nanomolar to picomolar levels, with dissolved iron concentrations decreasing sharply after each infusion. The rate of this iron disappearance increased progressively from the first to third infusions. The vast majority of the added iron occurred in the colloidal phase, with soluble (< 1 kDa) concentrations increasing by only ~ 25 pM over ambient levels. The percentage of colloidal iron decreased from nearly 100% immediately following the first infusion to ~60% 9 days later. Colloidal-sized iron phases continued to dominate iron speciation even when total dissolved iron concentrations within the patch fell to near pre-release levels.

Soluble iron concentrations increased from 16 to ~ 40 pM Fe over the four days following the first infusion. This trend preceded increases in Chl-*a* concentrations by 2 full days. After biomass (as indicated by Chl-*a*) began to increase dramatically on Day 5–6, soluble iron concentrations dropped precipitously and then remained at near pre-release levels through Day 9, the final day of CFF sampling.

The relative drawdown rate of nitrate and silicic acid provides some insight to the level of iron stress experienced by diatoms within the patch. The silicic acid:nitrate ratio in surface waters was 0.5 before infusion began. Alleviation of iron limitation by infusion led to an initially balanced drawdown of nitrate and silicic acid. But approximately 1.5 days after the second infusion the Si:N drawdown ratio increased significantly, with the subsequent linear decrease in dissolved Si:N ratios being synchronous with decreased soluble iron concentrations and increases in Chl-*a*. A minimum dissolved silicic acid:nitrate ratio of 0.14 occurred on Day 13 after Chl-*a* concentrations peaked before beginning to increase again in conjunction with decreasing Chl-*a* concentrations.

Discussion

Some insight to the minimum level of iron needed to generate massive diatom blooms comes from size-fractionated analysis of iron within the infused patch during IronEx II. Although there remains uncertainty about which iron species are available to phytoplankton in general, and diatoms in particular, iron uptake appears to be restricted to the truly soluble, or low molecular weight fraction in seawater (Wells *et al*., 1995). The colloidal proportion of added iron was initially extremely high (99%) but decreased somewhat with each infusion (90% in the second infusion; 60% in the third infusion). However, this progressive change is largely due to the decreasing concentrations of total dissolved iron measured in the samples obtained after each infusion. This trend may be simply due to the non-homogeneous distribution of

iron within the patch, but it also is likely that the increasing iron demand by the rapidly growing population resulted in higher short-term rates of iron removal from the dissolved phase.

Soluble iron concentrations (or that containing the iron species known to be directly accessed by phytoplankton) doubled after the initial iron infusion and continued to increase over the first 4 days, reaching a maximum of ~ 40 pM Fe. During the same time, total Fe(III) complexing organic ligands increased by 400% to ~ 2 nM, with most of the increase attributed to the stronger ligand class (Rue and Bruland, 1997). The bulk of these iron–ligand complexes were colloidal in size, in contrast to pre-release conditions where the strong ligand–iron complexes were largely in the soluble phase. The increase in soluble iron concentrations during the first 4 days presumably reflects a small change in the size distribution of these ligands with time, through either the biotic release of low molecular weight iron complexing ligands or by the escape of low molecular weight ligands from colloidal polymer matrices (Chin *et al*., 1998).

A dramatic decrease in soluble iron concentrations was observed on Day 6, likely due to the rapidly increasing iron demand, as evidenced by the increasing Chl-*a* concentrations across this interval. The total iron demand can be estimated from Chl-*a* concentrations and cellular iron quotas measured for oceanic diatoms under controlled conditions. Chl-*a* increased within the patch by ~ 3 μg L^{-1} over the first 9 days, corresponding to an increase in cellular carbon of ~1.7 $\times 10^{-5}$ moles C L^{-1} (0.20 mmol Chl:mol C (Sunda and Huntsman, 1995)). Taking a lower value for the cellular Fe:C ratio for oceanic diatoms (5 μmol Fe:mol C, Sunda and Huntsman, 1995) yields a minimum cellular iron demand of ~90 pM Fe to fuel the increase in Chl-*a* measured. This value underestimates actual demand because neither grazing nor "luxury" uptake of iron by cells is taken into account. It is clear then that significant iron flux from the colloidal through the soluble phase was required to support bloom development.

Assessing what iron flux to surface waters is required to stimulate large diatom blooms like that generated by IronEx II reduces to two issues: (1) what is the lowest iron concentration whereby uptake still permits maximum cellular growth rates, and (2) what iron flux to surface waters is then needed to sustain high diatom productivity once this concentration threshold is surpassed? The distinction between concentration and flux is important because it constrains the magnitude of events needed to generate intense diatom blooms. The minimum iron concentration at which pennate diatom growth becomes diffusion limited was estimated as a function of cell length and cell shape. The parameters chosen for this calculation were a molecular diffusivity of 0.9×10^{-5} cm^2 s^{-1} (for iron species sized near inorganic complexes), a cellular iron content of 50 μmoles L^{-1} of cytoplasm (Sunda and Huntsman, 1995), a cellular aspect ratio of 20 (length/width) and a growth rate of 1 d^{-1} (K. Bares, pers. comm.). The result illustrates the extreme benefit pennate diatoms enjoy over their centric cousins with respect to diffusional constraints. To escape diffusion-limited growth conditions, centric diatoms 15 μm in diameter require > 160 times higher iron concentrations than pennate diatoms 15 μm in length. This difference might help explain why centric diatoms flourished in some bottle enrichment studies with equatorial Pacific waters (Maldonado and Price, 1996) while pennate species dominated in the mesoscale experiment; iron availability in the bottles would have remained comparatively high because iron was not lost from the system.

The question of the iron flux needed to sustain high diatom productivity (once diffusion limitation concentrations are surpassed) is more complex. While the iron flux used during IronEx II was massive (compared to ambient inputs), and the resultant diatom response dramatic, there is reason to suspect that growth rates in the patch remained below maximum levels. Growth rates of oceanic diatoms in controlled culture conditions reach ≥ 1.5 d^{-1} (Sunda and Huntsman, 1995; Maldonado and Price, 1996), significantly higher than the growth rate estimated during the bloom (1 d^{-1}, K. Bares, pers. comm.). Indeed, there is evidence that diatoms were experiencing iron stress in the midst of bloom development. It has been shown recently that diatoms draw down nitrate and silicic acid equally under iron-replete conditions, but iron stress causes a shift to the preferential removal of silicic acid (Hutchins and Bruland, 1998). By this measure, the low ambient nitrate:silicic acid ratio (~0.5) indicates the influence of iron limitation prior to the first iron infusion. The subsequent utilization of these nutrients begins equally shortly after infusion but the drawdown ratio then drops

sharply as Chl-*a* increases, and soluble iron concentrations decrease. These findings strongly indicate that the bloom organisms had become iron stressed despite the third iron infusion on Day 7. These data add further support to the finding that diatoms were unable to access all of the iron in the soluble phase. As a result, the geochemical impact of the bloom on nitrate drawdown and the carbon cycle was smaller that it would have been if silicic acid utilization had been more efficient.

Despite our uncertainty about the iron forms that phytoplankton access in seawater, the results here demonstrate that concentrations of soluble iron complexed by natural organic ligands need only increase slightly (≤ 25 pM) above ambient levels for large diatoms to grow rapidly. However, what is not clear is whether the increase in strong Fe(III) complexing organic ligand concentrations that accompany large influxes of iron ultimately result in lower effective supply of iron to diatoms and other large eukaryotic organisms. If so, then slow, persistent influxes of iron may not be able to maintain high diatom growth once the chemical speciation of iron again becomes dominated by complexation with strong organic chelators.

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Characteristic vertical profiles of Fe(III) hydroxide solubility in the northwestern North Pacific Ocean

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Recently, a number of studies pointed out that the Fe(III) complexation with natural organic ligands is possible in oceanic waters, but the detailed vertical distribution, origin and chemical identity of organic ligands are largely unknown. Here, we report the spatial vertical distributions of Fe(III) hydroxide solubility in subarctic and subtropical water masses and the boundary zone in the northwestern North Pacific Ocean. The detailed vertical profiles of Fe(III) hydroxide solubility have the following features in common:

- the solubility in the surface mixed layer (0–50–100 m) is generally high and variable (0.3–1.9 nM);
- the solubility minima (0.2–0.4 nM) occur at depths of 75–125 m, below the suface mixed layer;
- the subsequent solubility levels in middepth waters appear to increase with depth in association with the increase in nutrient concentrations in the subtropical and boundary zone (0.2–0.7 nM) or to vary little with high constant solubility (0.7 nM) and nutrient values in the subarctic zone (upwelling area);
- the solubility levels in deep waters (>1000–1500 m) tend to decrease a little to 0.4–0.5 nM with depth in association with the decrease in nutrient concentrations.

The higher Fe(III) hydroxide solubility in the surface mixed layer is probably due to higher concentration or stronger affinity of natural organic Fe(III) chelators, which were possibly released by phytoplankton or bacteria during their metabolism. There are significant correlations between the Fe(III) hydroxide solubility and the nutrient (PO_4, NO_3+NO_2) concentration in deeper waters below the depth of minimum solubility, suggesting the regenerative formation of organic Fe(III) chelators through oxidative decomposition and transformation of biogenic organic matter sinking into the deep waters.

A1.2.3 Biology in the North Pacific and IronEx

Station Papa time series: Insights into ecosystem dynamics

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Ocean Station Papa (OSP) in the subarctic NE Pacific at 50°N and 145°W, has been the site of open ocean research for the last 40 years, commencing with sampling conducted on board the Canadian weatherships from 1956–1981. Hydrocasts were carried out to a depth of 1200 m at OSP. In 1959, 5 stations were sampled along the line connecting OSP to the coast (Line P) and by 1964, 13 stations along Line P were established. During the 25-year weathership era, temperature, salinity, nutrients (nitrate, phosphate and silicate), Chl-*a* and zooplankton were sampled approximately weekly (but with considerable variability). This good temporal coverage firmly established the annual cycle at OSP. This cycle is provided in some detail by Whitney and Freeland (1999), and only the highlights are summarized here. The range in selected parameters is given in Table 1. In the winter, winds average 12 m s^{-1} and the surface waters are mixed to about 120 m (much shallower than the Atlantic Ocean where mixing occurs to about 300 m). Surface temperature reaches a minimum of 5–6°C, salinity increases to 32.7 and maximum winter nitrate and silicate are 15.8 ± 2.3 and 24.0 ± 3.4 µM, respectively. Winter Chl-*a* is approximately 0.2–0.3 µg L^{-1}. The mean irradiance levels received by cells traversing the mixed layer is 0.91 and 2.3 mol quanta m^{-2} d^{-1} in February and October, respectively (Maldonado *et al*., 1999). As incident irradiance increases and the mixed layer depth (MLD) decreases in spring, Chl-*a* increases from 0.2–0.4 µg L^{-1} (there is no spring bloom as observed in the Atlantic Ocean). It is interesting that nitrate drawdown begins in April, while silicate begins to decline in early June. Sediment traps at 200 m depth show the highest downward flux of Si from June to July, whereas N fluxes are high from May through September (Wong *et al*., 1999). In August/September, when the MLD is only 40 m and surface temperatures reach 12–13°C, nitrate and silicate reach minimal values of about 8–9 and 13 µM, respectively. This represents a drawdown in nitrate and silicate of 7 and 11 µM, respectively, and a Si:N drawdown ratio of 1.6:1. This ratio suggests iron limitation since it is higher than the normal 1:1 Si:N ratio (Hutchins *et al*., 1998).

At the end of the weathership era, three key observations were used to explain how the ecosystem functioned. Since there was no spring bloom and minimum summer nitrate values were 8–9 µM (not 0), it was suggested that the large copepods which migrated to the surface and grew quickly in size, controlled the phytoplankton standing crop via grazing (*i.e.*, top down control) and aided secondarily by low light (Parsons and Lalli, 1988). This conclusion was logical because it was before the realization of the importance of small phytoplankton (picoplankton) and microzooplankton, and the discovery of iron limitation.

In the mid-1980s, the Subarctic Pacific Ecosystem Research (SUPER) group challenged the "major grazer hypothesis" (Frost, 1987). They found that the main diet of these large copepods (*Neocalanus* spp. and others) was not phytoplankton. They were mainly carnivores and they consumed only small amounts of phytoplankton (Dagg, 1993). In addition, Booth *et al*. (1993) found that phytoplankton < 5 µm dominated the phyto-plankton standing stock. Just as the field work by SUPER was ending, Martin and his colleagues made the startling discovery that iron limited primary productivity at OSP (Martin and Fitzwater, 1988). Therefore, within a few years these three new key observations dramatically revised our ideas of how this ecosystem functioned.

Table 1 Range in various ecosystem parameters at OSP, with winter representing one extreme and late summer the other extreme. Most values are for surface water or integrated over the photic zone.

Parameter	Winter	Late summer	Reference
Light Extinction Coeff (k, m^{-1})	0.065	0.13	Sherry *et al.*, 1999
Wind (m s^{-1})	12	7	Whitney and Freeland, 1999
Temperature (°C)	5.5	13	Whitney and Freeland, 1999
Salinity	32.7	32.5	Whitney and Freeland, 1999
$Sigma_t$	25.7	24.5	Whitney and Freeland, 1999
Mixed Layer Depth (m)	120	40	Whitney and Freeland, 1999
Photic Zone (m)	80	30–40	Sherry *et al*., 1999
Nitrate (µM)	15.8	8.5	Whitney and Freeland, 1999
Silicate (µM)	24.0	13.0	Whitney and Freeland, 1999
Phosphate (µM)	0.8	1.3	Appendix, DSR II **46**: 3019
Ammonium (µM)	0.5	0.1	Varela and Harrison, 1999
Urea (µg-at L^{-1})	0.5	0.1	Varela and Harrison, 1999
Fe (nM)	~ 0.1	0.05	Nishioka, Wong and Tabata (unpubl. data)
chl (µg L^{-1})	0.2	0.4	Boyd and Harrison, 1999
chl (mg m^{-2})	13.5	20	Varela and Harrison, 1999
Phytoplankton Carbon (µg C L^{-1})	15	25	Denman and Putland (unpubl. data)
POC (µg C L^{-1})	50	70–90	Wong *et al.*, 1999
Particulate N (mg-at m^{-2})	52	95	Varela and Harrison, 1999
Primary Productivity (µg C L^{-1} d^{-1})	<10	35	Boyd and Harrison, 1999
Primary Productivity (mg C m^{-2} d^{-1})	300	400–850	Wong *et al*., 1995; Boyd and Harrison, 1999
f-ratio	0.25	0.25	Varela and Harrison, 1999
ρ NO_3 (mg-at m^{-2} d^{-1})	1.78	3.86	Varela and Harrison, 1999
ρ urea (mg-at m^{-2} d^{-1})	0.96	3.59	Varela and Harrison, 1999
ρ NH_4 (mg-at m^{-2} d^{-1})	3.23	5.80	Varela and Harrison, 1999
ρ total N (mg-at m^{-2} d^{-1})	5.96	13.35	Varela and Harrison, 1999
Bacterial Biomass (µg C L^{-1})	12	25	Sherry *et al*., 1999
Bacterial Productivity (µg C L^{-1} d^{-1})	0.4	2.2	Sherry *et al*., 1999
Mesozooplankton (mg C m^{-3})	3	20	Goldblatt *et al*., 1999

By the beginning of the Canadian JGOFS (Joint Global Ocean Flux Study) project in 1992, the issue of iron limitation was not resolved, specifically the iron limitation versus grazing debate, because the large grazers were usually excluded from the previous bottle experiments (Banse, 1990; Miller *et al*., 1991; Frost, 1991; Miller, 1993). During the early 1990s, further shipboard iron enrichment experiments by Boyd and colleagues confirmed that iron limitation did limit phytoplankton stocks despite the presence of mesozooplankton levels comparable to the highest *in situ* upper ocean levels observed at OSP (Boyd *et al*., 1999). Furthermore, the iron enrichment in carboy experiments facilitated the drawdown of nitrate in May and September (Boyd *et al*., 1996). When iron was added in their experiments, large predominately pennate diatoms (> 18 µm) grew, confirming Martin and Fitzwater's (1988) earlier observations. This result was surprising since oceanic pennate diatoms were usually considered to be a minor component of oceanic phytoplankton assemblages. Iron limitation was also confirmed by biophysical (F_v/F_m fluorescence ratio, Boyd *et al*., 1998a) and biochemical (an iron-mediated reduction in the expression of the molecular marker for iron limitation, flavodoxin; LaRoche *et al*., 1996) markers. In February, when Boyd added iron, little or no increase in Chl-*a* was observed after a 5-day incubation, and it was suggested that light may be a co-limiting factor along with iron (Boyd *et al*., 1996). This suggestion was later confirmed by Maldonado *et al*. (1999) who demonstrated co-limitation of phytoplankton growth by iron and light during winter at OSP.

Ammonium showed little seasonality with concentrations ranging from 0.1 to 0.5 µM

(Table 1). Urea concentrations were generally from 0.1 to 0.5 µg-at L^{-1}, except for May 1993 when surface urea was 0.8 and up to 2.0 µg-at L^{-1} at 40 m (Varela and Harrison, 1999). Nitrate, urea and ammonium uptake rates in winter (February/ March) were 1.8, 1.0, and 3.2 mg-at N m^{-2} d^{-1}, respectively; in spring (May) they were 2.7, 3.3 and 5.4 and in late summer (September) they were 3.9, 3.6 and 5.8 mg at N m^{-2} d^{-1}, respectively. The seasonally averaged depth- integrated absolute uptake rates were 27% nitrate, 23% urea and 50% ammonium. There was no significant difference in the annual trend for the depth-integrated *f*-ratio, and the seasonal average was 0.25. Phytoplankton utilized nitrogen in the following order; NH_4 >> NO_3 > urea. The *f*-ratio was overestimated by up to 36% when urea was excluded from the calculation (Varela and Harrison, 1999).

There is low seasonality in primary productivity with mean winter and spring/summer values of 300 and 800 mg C m^{-2} d^{-1}, respectively (Boyd and Harrison, 1999). Using Wong *et al.*'s (1995) fall values of 366 mg C m^{-2} d^{-1}, and the values by Boyd and Harrison (1999) above, yields an annual estimate of 215 g C m^{-2} y^{-1} which is somewhat higher than Wong *et al.*'s (1995) estimate of 140 g C m^{-2} y^{-1} and Welschmeyer *et al.*'s (1993) estimate of 170 g C m^{-2} y^{-1} (using Wong's winter values) (Harrison *et al.*, 1999). This annual primary productivity is quite high considering that OSP is similar to an oligotrophic gyre with nutrient (Fe) limitation, a phytoplankton assemblage dominated by small cells and the primary productivity based largely on regenerated nutrients (*f*-ratio = 0.25).

The dominant small phytoplankton grow at 0.1 to 0.8 d^{-1}, similar to the growth rate of many microzooplankton (Landry *et al.*, 1993; Boyd and Harrison, 1999). Therefore, it has been suggested that these small phytoplankton are controlled by microzooplankton grazing (Landry *et al.*, 1993), although results suggest that these micro-zooplankters preferentially ingest heterotrophic rather than autotrophic picoplankton (Rivkin *et al.*, 1999). The large copepods such as *Neocalanus* sp. are now known to be omnivores rather than herbivores (Dagg, 1993). In fact, when twice the maximum ambient number of *Neocalanus plumchrus* was added to a carboy enriched with iron, large pennate diatoms grew and they were not grazed down by high abundances (comparable to the maximum ambient levels) of the large copepods (Boyd *et al.*, 1999).

In contrast to the conceptual phytoplankton–mesozooplankton food chain previously reported (Frost, 1987; Parsons and Lalli, 1988), now it is necessary to have two nitrogen sources and two size fractions of phytoplankton to explain the ecosystem dynamics at OSP. The large phytoplankton are thought to exhibit bottom up control by iron (due to their higher iron cell quotas; Muggli *et al.*, 1997), while the small phytoplankton exhibit top down control by microzooplankton grazing. The large phytoplankton (mainly diatoms > 10 µm) increase in abunadance quickly when iron is added in carboy experiments and they are able to use up all the ambient nitrate. They are not eaten to any marked extent by *N. plumchrus*, and thus these large cells likely sink out after they consume the iron addition (Muggli *et al.*, 1996). The small phytoplankton (mainly prasinophytes and prymnesiophytes < 5 µm) utilize regenerated nitrogen (NH_4 and urea, Boyd *et al.*, 1996; Varela and Harrison, 1999) to decrease the iron demand associated with nitrate reduction to ammonium.

Microzooplankton span a wide size range and taxonomic group of organisms and, to date, they have not been well studied. They consume mostly small phytoplankton and bacteria (Landry *et al.*, 1993; Rivkin *et al.*, 1999). Their biomass shows little seasonality, unlike the 5- to 10-fold increase in mesozooplankton in May/June (mainly due to the increase in size of the C1 to C4 copepodites (Boyd *et al.*, 1995, see their Table 1). Therefore, the nearly 3-fold seasonal increase in primary productivity from winter to summer (Boyd and Harrison, 1999) is passed through the microzooplankton to provide part of the large increase in mesozooplankton biomass in May/June.

Mean monthly downward particle fluxes at 3800 m show a distinct seasonality. Flux rates of 38 mg m^{-2} d^{-1} (in February) have an annual minimum during winter months and a maximum of 150 mg m^{-2} d^{-1} during summer. The average downward mass flux at OSP is 52 g m^{-2} y^{-1} at 1000 m and 32 g m^{-2} y^{-1} at 3800 m (Wong *et al.*, 1999).

Interannaul variability

A warming of 1.2°C/century and freshening of 0.2 psu/century in the surface waters at OSP has been

estimated by Freeland *et al.* (1997). From these data, they calculated that the MLD has also decreased significantly ($p = 0.05$) from 130 m in the 1960s to 100 m in the late 1990s. This decrease in the MLD likely contributes to the decrease in the winter nutrient concentrations.

In addition to these longer-term changes, El Niño events have resulted in rapid, short-lived changes. One of the strongest El Niño events of the century happened in 1982/83. During that time the largest particle flux to sediment traps at 3800 m occurred and 90% of this flux was opal; the particle flux was > 400 mg m^{-2} d^{-1} during late summer (Wong and Matear, 1999).

During the transition from the La Niña in 1989 to the series of El Niños ending in 1994, the surface waters became warmer by 2°C, more saline by 0.3 psu and the winter nitrate concentrations were 30% lower (Whitney *et al*., 1998). In late summer, depletion of nitrate in the surface waters during the 1989 La Niña period extended 250 km offshore, but during the 1994 El Niño period, surface nitrate depletion extended 600 km offshore. This suggests that the boundary between the more coastal nitrate-limited area and the iron-limited offshore area can shift more offshore or onshore due to El Niño/La Niña events. The lower winter nitrate supply during El Niño is estimated to have reduced new production by 40% and possibly shifted phytoplankton community structure to smaller primary producers (and a longer food chain) which could, in turn, have affected higher trophic levels (Whitney *et al*., 1998).

Whitney and Freeland (1999) compared the nitrate and silicate concentrations of the 1970s to the 1990s and observed that the winter nitrate has decreased by 2.5 µM and silicate by 3.6 µM. Their nutrient utilization between February and September has declined from 7.8 to 6.5 µM NO_3 and from 8.5 to 6.0 µM Si (the $Si:NO_3$ ratio decreased from 1.08 to 0.92). The larger decrease in silicate uptake (29%) relative to the decrease in nitrate uptake (17%) suggests that the supply of iron may also have declined during these two decades because the Si:N uptake ratio for phytoplankton increases under iron limitation (Hutchins *et al*., 1998).

From 1956 to 1980 the mesozooplankton biomass has nearly doubled at OSP (Brodeur and Ware, 1992). An obvious question is: Has the phytoplankton biomass/productivity also increased? There has been no apparent increase in Chl-*a*, despite the fact that GF/F filters (0.8 µm nominal pore size) were used in the 1990s compared to GF/C filters (1.8 µm nominal pore size) in the 1960s–70s. However, early estimates of an annual primary productivity of 60 g C m^{-2} (McAllister *et al*., 1960) have increased to 140 g C m^{-2} (Wong *et al*., 1995) and recently to 215 g C m^{-2} (Harrison *et al*., 1999). This 2- to 3-fold increase in primary productivity may be due to the use of trace metal clean techniques in the 1980s and 90s, but the increase could be real and it could explain the doubling in the mesozooplankton biomass.

The other long-term change in mesozooplankton is the arrival time of *N. plumchrus* into surface waters 2 months earlier than in the 1960s–70s (Mackas *et al*., 1998). The peak biomass (late C4 copepodites) now occurs in early May versus early July. The reason for this earlier shift in this copepod's life cycle in unclear, but it may be linked to the presently warmer surface waters.

Interannual variation in nitrate and silicate was well documented in the 1970s due to the weekly sampling by weathership personnel. During the summers of 1972, 1976 and 1979, silicate was depleted to < 1 µM, indicating that productivity was high and dominated by diatoms (Wong and Matear, 1999). Both 1972 and 1976 were high silicate and nitrate utilization years, while 1976 had low nitrate utilization relative to silicate utilization ($Si:NO_3$ drawdown = 3.6); the only way to explain this high ratio at present is to suggest severe iron limitation. Unfortunately, during the decade of the 1970s no sediment traps were deployed to assess changes in export to depth.

During brief periods of 1964, 1965, 1969 and 1975, Chl-*a* concentrations were 10 times greater than ambient concentrations (*i.e.*, > 3 µg L^{-1}; Parslow 1981). One explanation for these Chl-*a* peaks is the episodic input of iron, based on the observations during iron addition experiments where pennate diatoms grow and draw down nitrate and silicate. Again, it would have been helpful to have had sediment traps to determine if this 10-fold increase in Chl-*a* resulted in increased particle fluxes (see Boyd *et al.* (1998b) for further discussion). Surprisingly, the detailed time series of nitrate and

silicate concentrations in 1975 do not show accompanying drawdowns in nitrate and silicate during the three peaks in chlorophyll.

Summary

The 40-year time series at OSP provides a valuable data set to resolve the ecosystem dynamics in this region. The range of various ecosystem parameters at OSP is summarized in Table 1. During 1956–81, the temporal resolution was excellent, however, the number of parameters that was measured was limited. There was no size-fractionated Chl-*a*, no microzooplankton biomass estimates, and no sediment traps deployed. The lack of these data limits the interpretation of unusual years. For example, during 1972, 1976 and 1979 when silicate was drawn down to < 1 µM in the summer, the accompanying nitrate drawdown varied considerably and the Si:NO_3 drawdown ratios were 1.4, 2.5 and 3.6, respectively. Accompanying phytoplankton species composition data could help to clarify why these Si/N ratios varied by so much.

In the 1980s–90s, the number of parameters that was measured increased, but the temporal resolution decreased to two or three cruises per year. This may explain why many of the episodic events that were observed in the 1960s–70s (*e.g.*, Chl-*a* peaks and silicate drawdowns to < 1 µM) have not been observed since that time, except for the possible episode in 1983 when the largest particle flux to 3800 m sampled to date at OSP, was measured (Wong *et al.*, 1999).

Future research should continue regular cruises to maintain the priceless time series and include moored instruments to increase the temporal resolution in order to determine if any episodic events are presently occurring. Since iron limits algal growth, the sources of iron for OSP must be determined and these sources may be linked to the episodic increases in Chl-*a* or nutrient drawdown that were observed in the 1960s–70s (Boyd *et al.*, 1998b).

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East–west variability of primary production in the subarctic North Pacific derived from multi-sensor remote sensing during 1996–2000

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The two gyres in the subarctic North Pacific are known as the Western Subarctic Gyre (WSG) and the Alaskan Gyre (AG). Comparative studies on the primary production of the WSG and AG have been carried out in order to understand the different effects of iron in these two regions. Satellite monitoring of temporal–saptial variability of the chlorophyll *a* (Chl-*a*) distribution is very important for understanding the role of iron fertilization in HNLC (high nutrients, low chlorophyll) waters.

Objectives of this study are: (1) to find out the temporal and spatial variability of Chl-*a* distribution and primary productivity in the subarctic North Pacific, and (2) to understand the mechanisms regulating Chl-*a* distribution during 1996–2000. We worked with several multi-sensor remote sensing data sets, including ocean color by OCTS and SeaWiFS, sea surface temperature (SST) by AVHRR, and sea surface height by TOPEX/Poseidon. Ocean color and SST images were used to study interannual variablity of primary productivity and front dynamics. Sea surface height data were applied to study circulation, transport and eddy distribution. In addition to these satellite data sets, we generated estimated nitrate maps by the algorithm which employs satellite Chl-*a* and SST values. We attempted to calculate primary productivity by the modified Vertically Generalized Production Model (VGPM) (Behrenfeld and Falkowski, 1997) using ocean color and SST satellite data sets. On the other hand, we examined the estimation error of the SeaWiFS in-water algorithm using bio-optical data gathered by the R/V *Mirai* and other research vessels. As a result, the SeaWiFS in-water algorithm is working well in these regions with the error of less than 40 percent. East–west differences and year-to-year differences of primary production in the study area will be discussed.

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The planktonic nitrogen uptake and heterotrophic bacterial response during the second mesoscale Iron Enrichment Experiment (IronEx II) in the eastern equatorial Pacific Ocean

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The *in situ* responses of phytoplankton and hertertrophic bacteria were followed during the mesoscale iron enrichment experiment (IronEx II) conducted in the eastern equatorial Pacific during May–June, 1995. The rate of planktonic nitrogen (nitrate, ammonium and urea) uptake and the abundance and productivity of bacteria were measured within the fertilized patch and outside of the patch (control) at 15 m depth. Iron enrichment resulted in a dramatic increase in phytoplankton biomass (chlorophyll *a* concentration increased *ca*. 20-fold), but in contrast to long-term "grow-out" bottle experiments, the ambient nitrate concentration did not decrease to near zero, but declined by *ca*. 4–5 μM. Absolute uptake rates of nitrate increased *ca*. 15-fold as a result of iron enrichment, and post-incubation size-fractionation experiments demonstrate that larger phytoplankton (> 5 μm) were responsible for the enhanced nitrate utilization (> 85% of the NO_3 uptake). Iron enrichment shifted the size-structure of the phytoplankton community for picoplankton dominance to larger cells, and altered the relative utilization of new and regenerated N; the daytime *f*-ratio (*f*-ratio = NO_3 uptake/total N uptake) increased from *ca*. 0.65 to 0.91 (ratio uncorrected for isotopic dilution effects).

The carbon productivity and specific growth rate of heterotrophic bacteria increased 3-fold and 3- to 4-fold, respectively, resulting in the *in situ* accretion of bacteria (abundance increased 1.7-fold) within the iron patch. Although these results do not demonstrate a direct stimulatory response of hetertrophic bacteria to iron enrichment, they show that bacterial carbon demand can be potentially met by the increase in phytoplankton primary productivity.

Comparison of iron enrichment experiments on board in the NE and NW subarctic Pacific Ocean

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Introduction

It is recognized that iron plays a key role in controlling phytoplankton growth and primary productivity in the ocean, especially in HNLC (high nutrients, low chlorophyll) regions. The subarctic Pacific Ocean is one of them. We conducted three iron enrichment experiments on board in the summer of 1999 at Station Knot (NW) and Station P (NE) in the Pacific.

Materials and methods

Iron addition bioassays were conducted during the KH99-3 cruise (June 25 to August 25, 1999) of the R/V *Hakuho Maru*, University of Tokyo. Water samples were taken at two stations. The NW station (Stn K) and the NE station (Stn P) are located at the edge of the Western Subarctic Gyre (NW) and the edge of Alaskan Gyre (NE), respectively.

All necessary precautions were taken to prevent trace metal contamination throughout the preparation and handling. A specially designed bellows pump was used for pumping water from 5 m depth into Nalgene polycarbonate bottles (1 or 2 L).

The PC bottles were washed by a cleaning procedure. The samples were enriched iron as $FeCl_3$ at the final concentration of 0.3 or 1.0 nM. Some samples were also enriched zinc as $ZnCl_2$ at a final concentration of 1.0 nM. Nothing was added to the control bottles. The iron concentrations in the control bottles were confirmed to agree with that in the original seawater (Obata, pers. comm.). For the one experiment, five bottles were incubated for one treatment. The control incubation was conducted in duplicate while other treatments were single. The bottles were wrapped twice with plastic bags and incubated on board for 7 days in a water tank where water temperature was maintained to within 2ºC of the original temperature. All sample manupulations were conducted in a clean bench or clean room (Class 100) on board. Surface PAR (photosynthetically active radiation) was monitored with a 2 π sensor.

Nutrients and size-fractionated chlorophyll *a* (Chl-*a*) were measured every other day. Samples for bacteria and picoplankton counts were also taken at the same time. To prevent metal contamination, one bottle for each treatment was open for each sampling date to take subsamples for each measurement. Three different pore size nucleopore filters (10, 2 and 0.2 µm) were used for size fractionation of Chl-*a*. Nitrate reductase activity (NRA) and alkaline phosphatase activity (APA) were also assayed on Day 7.

Shipboard nutrient analyses were perfomed on a TRAACS 800 autoanalyzer, according to the methods of Grasshoff (1983). Chl-*a* was extracted with N-N, dimethylhormamide (Suzuki and Ishimaru, 1980) and measured with a Turner AU-10 fluorometer. NRA was assayed on board after Berges and Harrison (1995) in duplicate 500-ml samples on the initial day and on Day 7. Enzyme activity was expressed as a product of nitrite concentration per unit of volume and time (µmol NO_2 L^{-1} min^{-1}) or normalized to Chl-*a* concentration in the sample (µmol NO_2/µg Chl-a^{-1} min^{-1}). The APA was measured fluorometrically using 3-O-methylfluorescein phosphate as a substrate (Perry, 1972).

Phytoplankton cell counts were perfomed by light microscopy (larger cells: > 10 µm) and flow cytometry (smaller cells: < 10 µm). Samples for larger cells were preserved with formaldehyde at 5% of final concentration and stored at room temperature. Samples for smaller cells were preserved with paraformaldehide at 1% of final concentration and frozen immediately using liquid nitrogen and stored at –80ºC.

Results and discussion

Nitrate and phosphate concentrations at 5 m depth for both sites were almost the same, at 11 and 1.2 µM, while silicate was higher at Stn P (19 nM) than at Stn K (15nM). Total Chl-*a* concentration was slightly higher at Stn K than at Stn P, but both were below 0.5 µg L^{-1}, indicating both sites were at HNLC conditions at the time of the incubation. Light irradiance and temperature were not significantly different.

At both sites total Chl-*a* concentration increased sharply in the iron-enriched bottles after Day 3 (Fig. 1). At Stn K the highest Chl-*a* concentration of 8 µg L^{-1}, which was 17 times the initial value, was observed in the iron- and zinc-enriched bottle on Day 7. The increase in the bottle at 0.3 nM Fe was 4 µg L^{-1}, which was half of that at 1.0 nM Fe. The control bottles showed little increase in Chl-*a* in 7 days. The zinc-only addition did not affect Chl-*a* concentration as in the control. At Stn P the addition of iron also stimulated the Chl-*a* concentration to its highest concentration, at 14 µg L^{-1}, which was 52 times the initial value and observed in the iron- and zinc-enriched bottle on Day 7. The Chl-*a* concentration in the bottles at 0.3 nM Fe was almost a half of the 1.0 nM-enriched bottle. The control and Zn-only added bottles showed a slight increase in Chl-*a* of up to 3.5 µg L^{-1}. This increase was 18% of that in the 1.0 nM Fe-added bottles. These results strongly suggested that phytoplankton growth at both the NE and NW stations were limited by iron deficiency in the summer of 1999. This was supported by the evidence that dissolved iron was depleted in the surface at both stations (Obata, pers. comm.).

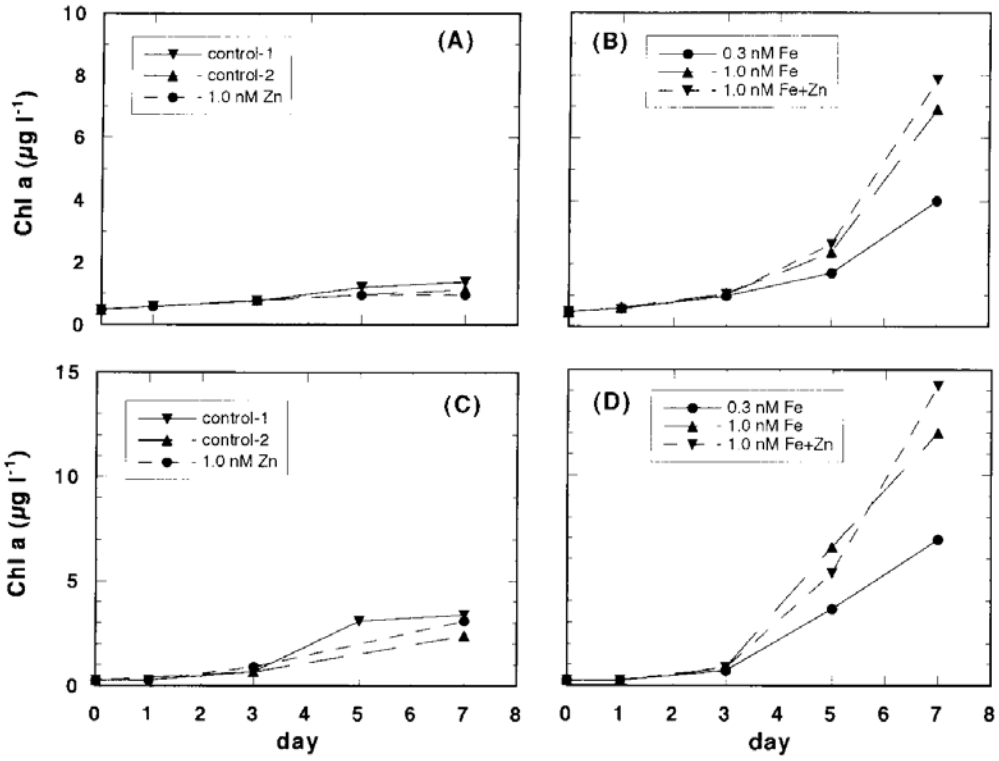

Fig. 1 Change in total Chl-*a* concentration with time in the incubation bottles. (A) two controls and 1.0 nM Zn-added bottles at Stn K (NW). (B) 0.3 and 1.0 nM Fe-added bottles and 1.0 nM Fe- and Zn-added bottles at Stn K. (C) same as in (A) except at Stn P (NE). (D) same as in (B) except at Stn P.

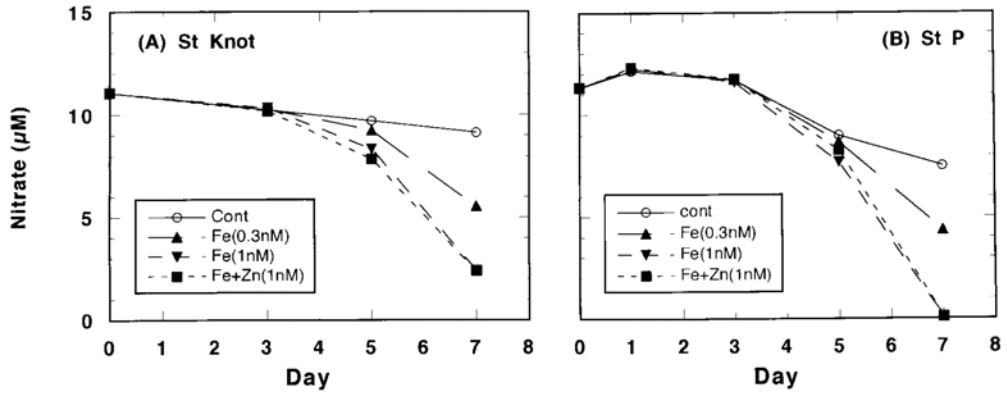

Fig. 2 Change in nitrate concentration with time in the incubation bottles. (A) Stn K (NW), (B) Stn P (NE).

Nutrient concentrations did not change until Day 3, but decreased after Day 5, especially for iron-added bottles (Fig. 2). The amounts of nutrient drawdown was higher for the 1.0 nM Fe addition than that for the 0.3 nM Fe addition and the control. No difference in phosphate and silicate concentrations on Day 7 was found between 1.0 nM Fe and 1.0 nM Fe plus 1.0 nM Zn-added bottles at Stn K, but iron- and zinc-added bottles showed higher utilization of nutrients at Stn P.

The consumed N:P ratio in the control bottles (12.5) was almost same in the iron-added bottles, but the Si:N ratio was 2.4 which was 2.2 times higher than in the iron-added bottles. The ratios in nutrient consumption were not different between the control and iron-added bottles at Stn P (Si:N ratio of 1.23 and 0.97 and N:P ratio of 8.8 and 10.5 in the control and the iron-added bottles). These differences in the consumption ratio of Si:N in the control bottles seemed to be derived from the different phytoplankton assemblages in each station: centric diatom dominance in the NW station and pennate diatom and coccolithophorids dominance in the NE station. The centric diatoms consumed silicate and nitrate at equimolar amounts under iron-replete conditions whereas they consumed more silicate than nitrate under iron-limited conditions (Takeda, 1998). *Emiliania huxleyi* are coccolithophorids that achieve their maximal growth rate even under iron-limited conditions (Muggli and Harrison, 1997). Thus, at Stn K dominant centric diatoms utilized much more silicate under iron limitation while at Stn P co-existing coccolithophorids and pennate diatoms utilized nutrients at a Si:N ratio of 1:1 even if the diatoms consumed excess silicate over nitrate, because coccolithophorids require only nitrate and phosphate as nutrients.

NRA measured on Day 0 at both stations was close to the detection limit. On Day 7, even after normalizing to Chl-*a* (biomass), NRA in the 1.0 nM Fe-added bottles showed 4 times higher activity than the control.

We also assayed APA which requires zinc for the same occasions as the NRA. None of the samples assayed showed detectable APA activity.

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Iron-siderophore receptors of heterotrophic marine bacteria

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Laboratory isolates of heterotrophic bacteria and field populations from low-iron waters of the ocean are able to take up ^{55}Fe from ferrioxamine B, a fungal siderophore (Granger and Price, 1999; Maldonado and Price, 1999). Rates of transport are up-regulated when ambient iron concentrations are low, suggesting that the use of siderophore-bound iron is an adaptation to overcome iron limitation. Using a non-denaturing PAGE (polyacrylamide gel electrophoresis) assay, we have discovered that the laboratory strains produce outer-membrane receptors that bind ferrioxamine B when iron is limiting growth. So far we have examined *Altermonas* sp., a clone isolated from waters near Station P in the subarctic Pacific Ocean, and PWF3, a clone from the Gulf of Mexico. The receptor is absent from cells cultured in a high-iron medium and is rapidly induced upon transfer to a low-iron medium. Its apparent molecular weight is roughly 80 kD, similar in the size to other siderophore receptors from terrestrial and pathogenic bacteria. We are now characterizing the specificity of the receptor(s) by examining binding of other siderophores and inorganic iron complexes. The method could be used to examine siderophore receptor expression in natural populations of bacteria before and during an iron fertilization experiment.

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The size-fraction of supplied iron and change in the concentration of iron in different size fractions in onboard bottle incubation experiments

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Introduction

The relationship between iron dynamics and phytoplankton growth is important for the study of iron biogeochemistry after iron fertilization. Size-fractionated iron analysis will be one useful approach for the study of iron dynamics. Therefore, to investigate the size-fraction of supplied iron and changes in the concentration of different size fractions of iron during phytoplankton growth in open-ocean seawater, a combination of measurements of size-fractionated iron and concurrent incubation experiments was performed at Ocean Station PAPA (OSP) in September 1997. One of the objectives of this experiment was to investigate the difference in iron size fractions in seawater between artificial iron addition and by natural iron supply.

Previous laboratory studies suggested that small colloidal particles formed in traditionally dissolved fractions (< 0.2 μm) might be one of the available iron forms for oceanic phytoplankton, with some mechanisms such as cell-surface reduction (Wells and Mayer, 1991; Wells *et al*., 1991; Kuma and Matsunaga, 1995; Nishioka and Takeda, 2000). Therefore, we investigated changes of size-fractionated iron during ambient phytoplankton growth by using a combined trace metal clean filtration method, which uses a 0.2 μm-pore size Teflon membrane filter and a 200-kDa nominal molecular weight polyethlene hollow-fiber ultrafilter (Nishioka and Takeda, 2000), and ultra-clean onboard bottle incubation experiments.

Method

An onboard incubation experiment was conducted on board the R/V *J.P. Tully* at Ocean Station PAPA (OSP: 50°N, 145°W) in September 1997. Seawater samples for vertical profiles of size-fractionated iron were collected using Teflon-coated, modified 30-L Go-Flo bottles suspended on a Kevlar line on September 3, 1997. For the incubation experiment, a water sample with resident phytoplankton was collected on September 4 from the sea surface and transferred to two acid-cleaned 20-L polyethylene tanks by rubber boat sampling with clean technique. A deep seawater sample was collected from 600 m depth using the same method as for the vertical sample collection on September 5. Acid-cleaned polycarbonate bottles were used for the incubation experiments. Although the problem with wall adsorption and desorption was expected, we confirmed that determination of dissolved and size-fractionated total acid-labile Fe concentration in filtered seawater samples did not significantly change in acid-cleaned polycarbonate incubation bottles for more than 5 days (Takeda and Obata, 1995; Nishioka and Takeda, 2000). We prepared three treatments in this incubation experiment.

Control treatment

Surface water was homogenized in a 20-L polyethylene bottle, and the water sample for the control treatment was then dispensed into eight, acid-cleaned, replicate 1-L polycarbonate incubation bottles.

Iron addition treatment

The iron-enriched treatment was prepared from surface water enriched with a 0.7 nM $FeCl_3$ solution and dispensed in the same manner as the control treatment after homogenization.

Deep water mixed treatment

For the deep water mixed (DWM) treatment, the surface water sample was placed in a 20-L polyethylene bottle enriched with deep seawater (surface water: deep water = 1:2) and then immediately homogenized. This mixed seawater was dispensed in the same way as for the control

treatment. These preparation procedures were done in a clean-air tent. The 1-L bottles were sealed in three plastic bags and then incubated on deck in running surface seawater baths to maintain surface seawater temperatures for 6 days. The incubation baths were covered with neutral density screens, and incubation light intensity was 27% of the ambient light level.

During the course of the incubations, two bottles for each treatment were withdrawn from the incubation bath at Days 2, 4 and 6 and submitted to the measurements of nutrients and Chl-*a* concentrations. Size-fractionated iron in each treatment seawater sample was determined on the initial and final days. Measured total labile Fe (unfiltered, detectable at pH 3.2) concentrations were divided into three size fractions; large labile particles (> 0.2 µm), small colloidal particles (0.2 µm–200 kDa) and soluble species (< 200 kDa). Concentrations of Fe (III) in the unfiltered and filtered samples were determined with an automatic Fe (III) analyzer (Kimoto Electric Co. Ltd.) using chelating resin concentration and chemi-luminescence detection (Obata *et al*., 1993, 1997). Initial sample bottles (Day 0) were analyzed without incubation. The incubation bottles were not repetitively sampled in order to avoid contamination during the sub-sampling procedure.

Results and Discussion

Vertical distribution of size-fractionated iron

At OSP, vertical profiles of dissolved Fe (< 0.2 µm) exhibited nutrient-like distributions in September 1997. Concentrations of soluble Fe were low in the surface mixed layer and increased below 300 m depth (~ 0.34 nM, Nishioka *et al*., 2001). The concentrations of small colloidal Fe were generally low in the surface mixed layer (0.01–0.06 nM) with higher concentrations below 200 m depth (~ 0.22 nM). At 600 m depth, small colloidal Fe represented 39% of dissolved Fe (< 0.2 µm) (Nishioka *et al*., 2001).

Onboard incubation experiment

Initial concentrations of nutrients, total Chl-*a* and total labile Fe in each treatment incubation bottle are shown in Table 1. In the DWM treatment, iron was enriched to 0.35 nM with a high level of nutrients. Both additions of minute $FeCl_3$ and Fe in deep water to surface seawater samples containing excess nutrients increased the stocks of Chl-*a* in incubation bottles relative to the controls (Figs. 1 and 2). Total Chl-*a* concentration in the control treatment increased by only 2.2 times the initial concentrations during 6 days of incubation. In contrast, total Chl-*a* concentrations in the iron addition treatment and DWM treatment increased 15 and 27 times, respectively for the initial concentrations in the same periods (Fig. 1).

The increase in Chl-*a* concentrations was correlated with major nutrient consumption (Fig. 2). In the iron addition and DWM treatments, concentrations of major nutrients were reduced significantly more than that of the control treatment. Nitrate concentration decreased only 0.7 µM in the control treatment, while 6.8 µM and 4.6 µM, respectively, in the iron addition and DWM treatments. Obviously, the stock of Chl-*a* concentration and nitrate consumption by phytoplankton taken from the OSP water increased with added $FeCl_3$ and deep water. These results strongly suggest that ambient phytoplankton were under iron limitation in OSP surface waters. Also, deepwater addition to surface water disarms iron limitation of ambient phytoplankton. This result suggests that biologically available iron is included in deep water and stimulates phytoplankton growth if deep water is supplied from below the mixed layer to the surface by upwelling and vertical diffusion.

Table 1 Initial (Day 0) concentrations of nutrients, total labile Fe and total Chl-*a* in each of the treatment incubation bottles.

	Unit	Control	Fe addition	Deep water mixed
NO_3	µM	7.7	7.7	32.1
PO_4	µM	0.77	0.77	2.29
Si	µM	14.7	14.7	82.3
Total labile Fe	nM	0.15	0.64	0.35
Total Chl-*a*	µg/L	0.33	0.33	0.09

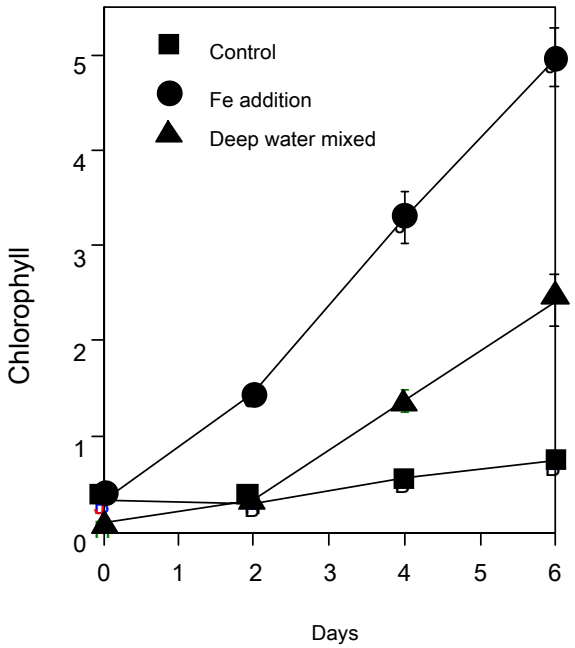

Fig. 1 The change of Chl-*a* concentration in each treatment.

Initial (Day 0) and final (Day 6) size-fractionated iron concentrations of all treatments are presented in Figure 3. In the control treatment, total labile Fe concentration decreased slightly (0.04 nM) during the 6 days, and significant iron remained in the only soluble species fraction (0.11 nM) in these bottles at end of the incubation. Total labile Fe concentration in the iron addition and DWM treatment samples showed large decreases during the 6 days' incubation. When the $FeCl_3$ solution was added to the OSP seawater in the iron addition treatment bottles, the iron concentration in small colloidal fraction increased significantly and comprised 85 % of the total labile Fe. Total labile Fe concentration decreased from 0.64 to 0.41 nM for the 6 days. Of the size-fractionated iron concentrations, small colloidal particles decreased significantly (0.43 nM) and 0.21 nM of this fraction converted to a large labile Fe fraction during incubation. Soluble Fe species did not significantly change on the final day (Fig. 3). While in DWM treatment, iron in the soluble species comprised 45.7 % of total labile Fe and total labile Fe concentration decreased 0.13 nM during 6 days of incubation. Of all the size fractions of iron, the soluble Fe species decreased most significantly by 0.11 nM. Comparing initial size-fractionated iron concentration in the iron addition treatment to the control treatment, the small colloidal Fe fraction decreased significantly during phytoplankton growth and some of the small colloidal Fe converted to the other fraction. The decrease in the small colloidal Fe concentration during the period of phytoplankton growth represented proportionally the greatest decrease in total labile Fe.

On the other hand, soluble Fe fraction increased in the DWM treatment at the initial stage of incubation and decreased during phytoplankton growth (Fig. 3). Comparing the iron addition treatment to the DWM treatment, the size fraction of supplied iron in seawater and its net change during phytoplankton growth were different. These results demonstrate that the size fraction of supplied iron in seawater and its net change during phytoplankton growth was different between different iron sources.

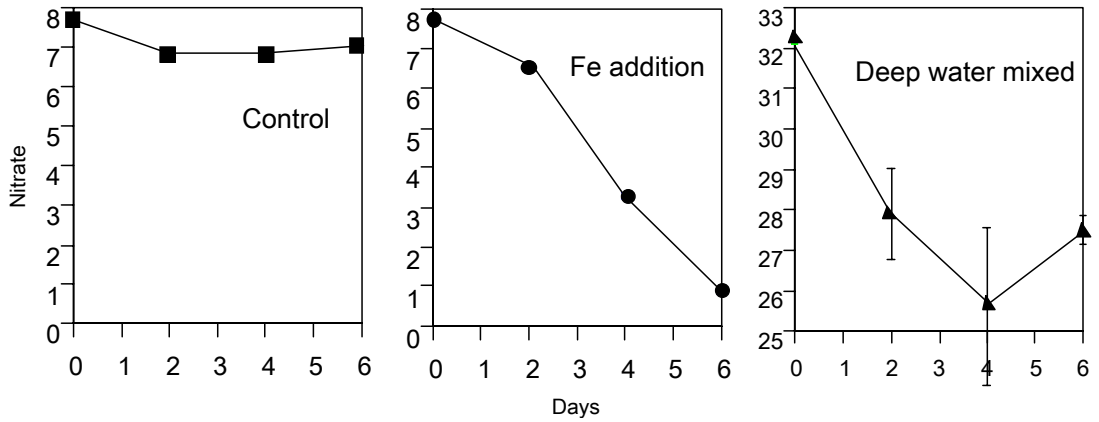

Fig. 2 The change of nitrate concentration in each treatment.

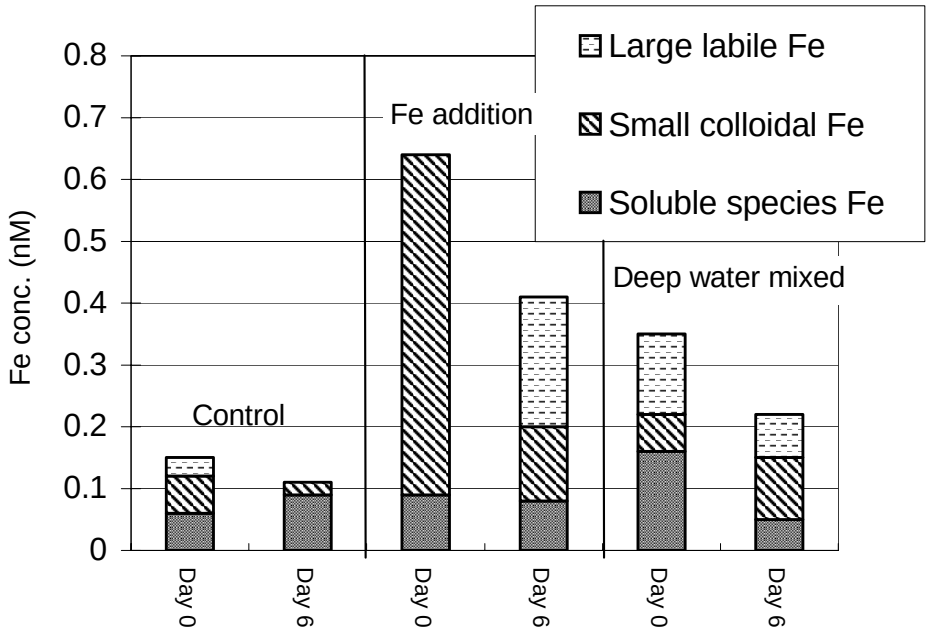

Fig. 3 Initial (Day 0) and final (Day 6) concentrations of size-fractionated Fe in each treatment.

Summary

- When the $FeCl_3$ solution was added to the surface seawater in the incubation bottle, the small colloidal Fe concentration increased significantly.
- The decrease in the small colloidal Fe concentration during the period of phytoplankton growth represented proportionally the greatest decrease in total labile Fe.
- Comparing the iron addition treatment to the DWM treatment, the size fraction of supplied iron in seawater and its net change during phytoplankton growth were different between different iron sources.
- The use of the size-fractionated iron analysis in iron fertilization experiments may provide important information for understanding iron dynamics after iron fertilization. Studies of iron dynamics in natural seawater should be focused on iron complexation with organic ligands as well as the relationship between changes in concentration of small colloidal Fe and phytoplankton growth.

Suggestions for iron fertilization experiments from this study

- Artificial iron additions result in different iron forms compared to the natural iron supply from deep water.
- Wet and dry deposition of atmospheric aerosols may have similar characteristics to the small colloidal Fe which is caused by artificial iron addition.
- The study of iron dynamics after iron fertilization should focus on iron complexation with organic ligands as well as small colloidal Fe.

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Zooplankton response to nutrient input

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The roles of grazers (microzooplankton and mesozooplankton) and remineralizers (bacteria and heterotrophic nanoflagellates) were estimated during a nutrient enrichment experiment using a mesocosm. Primary production increased by about 11 times during the initial 3 days, and the grazing rate by zooplankton also increased by 7.4 times. During the initial 5 days, the primary production exceeded the grazing rate and after that, almost balanced rates were observed. The biomass peaks of bacteria and heterotrophic nanoflagellates (HNF) were observed after the phytoplankton bloom declined. Bacterial production and HNF grazing gradually increased from the beginning to the end of the experiment. The contribution of microzooplankton to grazing was greatest during the initial 7 days, and the response to phytoplankton growth was fastest during the same period. Heterotrophic dinoflagellates were the most dominant component of microzooplankton, but naked ciliates showed the fastest growth in response to phytoplankton production. Overall, microzooplankton grazing contributed the most to phytoplankton depletion. Their response to the phytoplankton growth was very quick, and they removed about 50% of the primary production constantly. Thus, naked ciliates and heterotrophic dinoflagellates were the most plausible organisms to realize the steady state of phytoplankton concentration in the ocean.

The western subarctic Pacific is characterized by relatively high standing stocks of phytoplankton and mesozooplankton. Moreover, the dominance of diatoms and the almost complete absence of haptophytes characterize the phytoplankton community of the western subarctic Pacific Ocean. The expected difference in response to iron addition by lower trophic organisms between the east and west will be discussed.

A.1.2.4 Physics in the North Pacific and iron addition techniques

Physical processes affecting the distribution of iron-fertilized ocean water in the North Pacific

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Modification of the upper ocean occurs through a variety of physical processes, including wind and buoyancy forcing, advection, and turbulent diffusion. Proposed iron fertilization sites in the northwest and northeast Pacific are regions of marked upper ocean startification, slow eastward-flowing surface currents, and moderately weak turbulent dissipation. Mean surface currents in the region range from 1–5 cm/s (approximately 1–4 km/day) while the mean horizontal eddy viscosity ranges from roughly 1.5×10^7 cm^2/s in the meridional direction to 2.5×10^7 cm^2/s in the zonal direction. Decorrelation time scales for mesoscale (10 to 100 km) motions are around 2 to 3 days over associated spatial scales of 15 to 30 km. Although tidal currents are weak (diurnal and semidiurnal velocities are of order 1 cm/s) passing atmospheric fronts can generate strong (up to roughly 50 cm/s), rapidly varying currents of 16-h periods that persist for several days to a week. These currents, combined with turbulent wind mixing and surface buoyancy (heat) flux, lead to short-term (< 1 day) variability in the surface mixed layer depth and to the formation of seasonal pycnoclines above the permanent pycnocline (approximately 100 m depth). The experimental sites may be impacted by packets of internal tidal waves formed near the Aleutian Islands and by the passage of westward propagating mesoscale eddies generated along the west coast of North America. Coupled ocean–atmosphere circulation models can assist in the retrospective analysis of the iron plume dispersion but presently lack the spatial and temporal resolution for accurate experimental design and prediction.

The application of SF_6 tracer Lagrangian studies in iron fertilisation experiments

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Introduction

The physical mechanisms that determine the dispersion of biological populations in the surface ocean confound the determination of the limiting parameters and processes. Interpretation of Eulerian time series data is hindered by a lack of knowledge of the physical forcing, as any temporal change may simply reflect the advection of different water bodies past the sampling point. This has been addressed in Lagrangian studies of upper ocean biogeochemistry using drifter buoys (Harris *et al*., 1997). However, wind slippage may reduce the correlation between buoy and water body with time (Stanton *et al*., 1998), and drifter buoys are also restricted to the air–sea interface and so cannot track in the event of subduction. Dyes have been used successfully in dispersion studies (Smart and Laidlaw, 1977), but adsorption onto particles, toxicity, and limited real-time analytical capability restrict their application to short-term coastal and shelf seas. Sulphur hexafluoride (SF_6) can be used for tracking water bodies at the surface over periods of 2 weeks (Wanninkhof *et al*., 1997; Law *et al*., 2001), and periods exceeding a year for sub-surface releases (Ledwell *et al*., 1993, 1998). The benefits of SF_6 include high analytical sensitivity, low oceanic and atmospheric background, inertness and relatively low price, providing a favourable combination for mesoscale tracer studies in the open ocean with minimal volumes of SF_6 (Law *et al*., 1998). Tagging with SF_6 permits the monitoring of temporal change in a discrete body of water, so providing an observational tool for constraining biological and biogeochemical cycling rates in a non-perturbated system (Wanninkhof *et al*., 1997; Law *et al*., 1998). This capability further permits *in situ* manipulation of the water body, and so ameliorates the limitations of marine experimentation experienced in *in vivo* studies. The use of the tracer in these manipulation experiments confirms causality, as initially suggested by Watson *et al.* (1991) and subsequently demonstrated in the IronEx and SOIREE (**S**outhern **O**cean **I**ron **RE**lease **E**xperiment) studies (Martin *et al*., 1994; Coale *et al*., 1996; Boyd *et al*., 2000). In the following discussion, the SF_6 Lagrangian framework will be described and the benefits and limitations of this approach discussed.

Methods

Analytical methodology

Analytical detection limits of 0.02 fmol/kg (1 femtomole = 10^{-15} mol) and an extremely low surface water background concentration of < 1.4 fmol/l permit mesoscale water mass tracking with modest releases of SF_6 (50–120 g). The SF_6 patch is monitored using two different analytical systems for continuous measurement of the lateral dispersion at the surface and for discrete water sampling of the vertical dispersion. Both analyses are achieved using automated systems incorporating sparge-cryogenic trapping and detection of SF_6 by ECD (electron capture detector). The discrete system includes pre-sparge vacuum injection to accelerate stripping and shorten analysis time, a single trapping system, and handles large volumes (350 ml) with increased precision (<1%) (Law *et al*., 1994). The mapping system runs continuously, using sample volumes of 180 ml and a dual trapping system, with a minor reduction in precision and sensitivity (Upstill-Goddard *et al*., 1991; Law *et al*., 1998). A surface measurement is obtained every 3 min which, at a ship speed of 5–10 kts, gives spatial sampling every 0.45–0.9 km. Concentration data are incorporated in near real-time into an uncorrected plot of the areal distribution of the patch by integrating the SF_6 data with the ship's GPS position. This enables rapid alteration to ship speed and direction in response to variation in the SF_6 signal and ensures resolution of patch boundaries for determination of the "IN" and "OUT" patch sampling stations. A Lagrangian correction accounting for the advection of surface waters during mapping is subsequently applied.

Tracer release

The SF_6 saturation, release and surveying techniques are described in Upstill-Goddard *et al.* (1991) and Law *et al.* (1998). Briefly, a saturated solution is prepared by sparging surface seawater in a steel tank with pure SF_6 at a rate of ~120 ml/min. SF_6 saturation is monitored by Thermal Conductivity Detector (TCD). During the release, the SF_6-saturated seawater is pumped out with replacement by water above a diaphragm in the top of the tank to prevent SF_6 dilution or degassing. It is then mixed with the iron solution and released at mid-depth of the surface mixed layer through the outlet of a re-enforced tube which is attached to a weighted depressor. The optimal distance of the outlet is ~12–15 m behind the ship, so that the tracer/iron solution will be mixed by the prop wash while immediate loss of SF_6 to the atmosphere, caused by entrapment of air in the prop wash, is minimised. The release period and ship speed are dependent upon length of release track and sea state but vary between 3–5 kts and 8–16 h, respectively.

The release is generally preceded by a large-scale site survey of at least 50 km^2 to determine the suitability for a tracer experiment. The site should be free from dynamic influences such as fronts, and physical, biological and biogeochemical variability should be minimal. Depth of the mixed layer is a critical issue, as gas exchange may reduce the SF_6 signal rapidly in a shallow mixed layer (<15 m), whereas a deep mixed layer may lead to over-dilution of the tracer.

Correction for surface water advection is essential for the creation of a coherent tracer patch with a clearly definable centre. A dead-reckoning strategy was used in the initial tracer release experiments (Upstill-Goddard *et al.*, 1991; Law *et al.*, 2001), but the advection of the centre-point has been monitored more recently using surface drifter buoys in more recent experiments. These drifter buoys are equipped with a VHF packet radio which communicates the buoy GPS position to the ship at short intervals, and the drifter buoy also subsequently functions as a locator for mapping during excursions outside the patch. The drifter buoys are generally tethered to holey-sock drogues centred mid-depth of the surface mixed layer to reduce wind-slippage. However, wind drift may still occur, with deviation of the patch and buoy tracks on relatively short timescales (Law *et al.*, 1998; Stanton *et al.*, 1998), although this effect may be minimal (Law *et al.*, 2001; Martin *et al.*, 2001) (see Fig. 1).

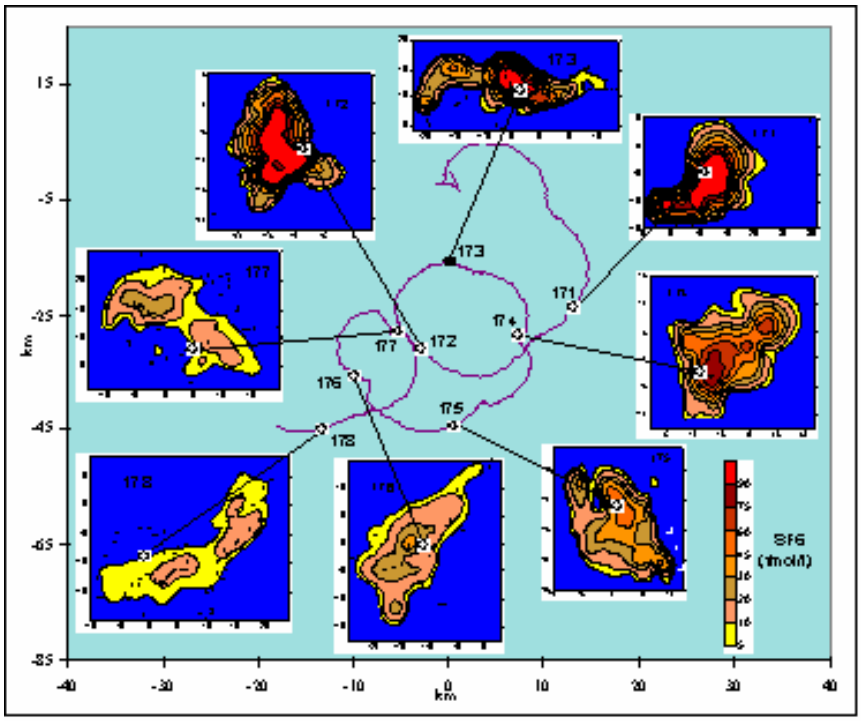

Fig. 1 GPS buoy track with transformed SF_6 contour plots for each day of survey referenced to the midday GPS buoy position from the UK PRIME Lagrangian experiment (Law *et al.*, 2001).

The SOIREE release was achieved by an expanding hexagonal track in a Lagrangian frame of reference around a central drifter buoy which updated its position every 10 min, with distances of 0.5–0.6 km between the expanding tracks (see Fig. 2). Re-infusion of iron was achieved using ADCP-derived velocities to inform the release track, with the SF_6 signal providing an indicator that the iron was added within the patch boundaries. This worked successfully during SOIREE as there was no need to add further SF_6 because the signal remained high. It is possible to use this approach during re-infusion of both SF_6 and iron (P. Nightingale, pers. comm.), although this runs the risk of contamination of the analytical mapping system.

Results and discussion

The Lagrangian tracer framework provides an "unbounded mesocosm" *in situ*, so that temporal variation can be determined within the same body of water, by comparison of the ecosystem response to the perturbation at the IN station with the control unperturbated OUT station. In addition, biogeochemical budgets benefit from concurrent determination of physical exchange rates in the water column and across the air–sea interface, accounting for loss processes and dilution.

Air–sea exchange rates

A minor disadvantage in the use of SF_6 as a tracer is its volatility, which reduces the time frame within which a surface release can be followed. The loss rate of SF_6 across the air–sea interface is well documented (Wanninkhof, 1992; Nightingale *et al*., 2000a), and can be estimated prior to release. Determination of the transfer velocity, k, in shelf seas and the open ocean has been achieved using a dual tracer approach of SF_6 and Helium-3 (Nightingale *et al*., 2000a). Estimates of k, obtained from wind-speed parameterisations (Liss and Merlivat, 1986; Wanninkhof, 1992) can differ by more than than 50%, and so lead to considerable variation in the calculated fluxes. The reliability of air–sea fluxes can be improved by concurrent determination of k and ΔC gradients for dissolved gases, as the k obtained will be representative of *in situ* conditions. In addition, constraining the volatile loss of SF_6 through the dual tracer approach will reduce the errors in the SF_6 budget and so improve dispersal and biogeochemical budgets. Furthermore, the addition of He-3 with SF_6 provides insight into the impact of other factors which influence k. For example, Nightingale *et al*. (2000b) have inferred from the IronEx II observations that the influence of algal blooms upon k is negligible.

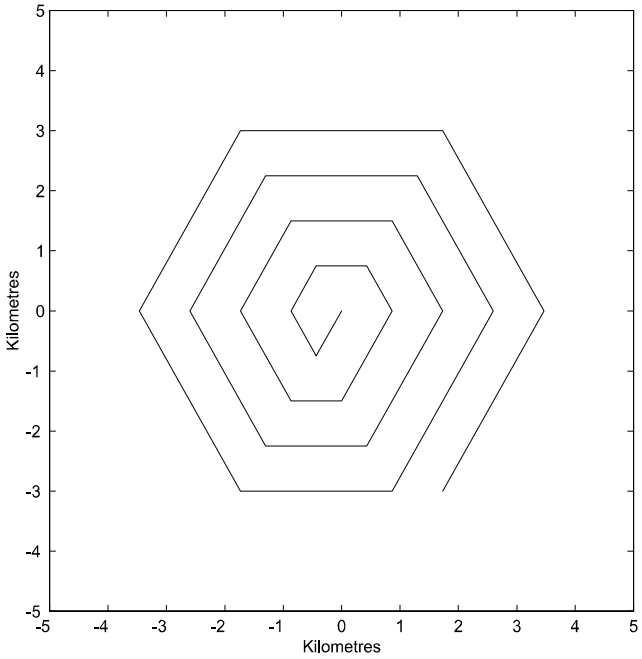

Fig. 2 Hexagonal release track around patch centre. Release pattern has a track spacing of 0.75 km. Patch area = 39 km^2, tacklength =52 km.

Lateral mixing and dispersion

Following the release, the total surface area occupied by the tracer initially expands rapidly as it mixes at the edges with water outside the patch. After this initial adjustment, the tracer will be normally distributed around the centre, and disperses at a slower rate. Calculation of the weighted second moment provides an estimate of the radial width of the tracer patch and, assuming Fickian diffusion, the lateral diffusivity Ky is then equal to half the gradient of the linear increase in W^2 with time (see Fig. 3). A recent estimate of Ky of 4 ± 2 m^2 s^{-1} during SOIREE in the Australasian sector of the Antarctic Circumpolar Current (Abraham *et al*., 2000) was within the range of 2–16 m^2 s^{-1} found at length-scale 8 km in dye release experiments in shelf seas (Okubo, 1980). However, this is lower than observed in previous open-ocean surface SF_6 releases, with a Ky of 22 ± 10 m^2 s^{-1} obtained within an eddy in the North Atlantic (Martin *et al*., 2001) and 25 m^2 s^{-1} in the equatorial Pacific (recalculated from Stanton *et al*., 1998).

Dispersion of the tracer is not just determined by diffusion. The spreading rate of a tracer patch in the streamline of an anti-cyclonic eddy exceeded that calculated from the radial effective horizontal diffusivity (Martin *et al*., 2001), due to shear-augmented along-streamline dispersion. The tracer patch area was estimated to increase by 5–26 km^2 d^{-1}, exceeding the surface area of 1.9 ± 0.86 km^2 d^{-1} which would result from an effectively diffuse dispersion in all directions.

In addition, the patch becomes influenced by strain and the length of the patch increases exponentially at the rate whereas the width of the patch stabilizes at a steady value. Stretching of the tracer patch results from the balance between the thinning effect of the strain and the widening tendency of diffusion. In ocean flows the strain is not constant, but an effective strain rate may be defined from the exponential growth in the length of a patch of tracer. The strength of the stirring in a two-dimensional flow can be estimated from the dispersion of the tracer, with calculation of an effective strain rate $\gamma = (8 \pm 3)\ 10^{-7}$ s^{-1} during SOIREE. This agreed with estimates of $\gamma = 5.8 \times 10^{-7}$ s^{-1} obtained from the subsequent dispersal of the patch as indicated by the chlorophyll distribution in satellite images (Abraham *et al*., 2000).

Dispersion will also influence any biological and biogeochemical variable within the patch the lateral and vertical transfer of the tracer provides a correction for this dilution. This was used to correct for the decrease in iron concentration due to dilution during SOIREE, thereby providing a constraint of the non-conservative losses of iron (Bowie *et al*., 2001).

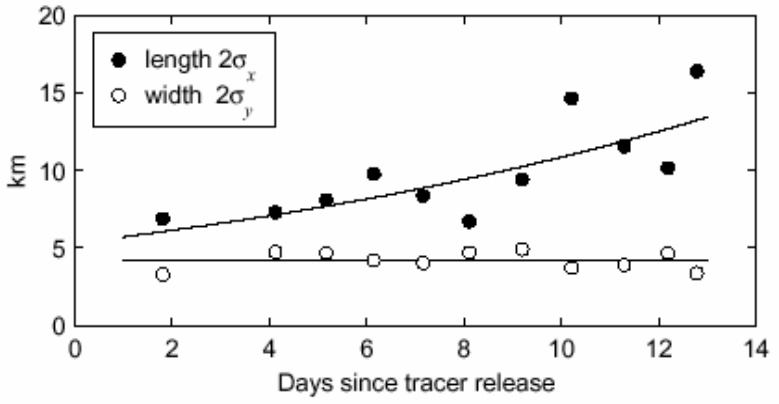

Fig. 3 Changes in the size and shape of the tracer patch during SOIREE. The width and length of the patch were determined by fitting a Gaussian ellipsoid using a least-squares fitting procedure. A best-fit to the length and width of the patch after Day 4 was used to estimate the strain rate and the diffusivity (Abraham *et al*., 2000).

Vertical diffusivity rates

The rate of transfer of SF_6 across isopycnals at the base of the mixed layer can provide a temporally and spatially integrated estimate of the vertical eddy diffusivity, K_z (Ledwell *et al.*, 1993, 1998; Law *et al*., 1998, 2001). The transfer of SF_6 across isopycnals results from the dissipation of turbulent kinetic energy by the breaking of internal waves and shear instability. As diapycnal diffusion of SF_6 is assumed to be Fickian, the distribution of SF_6 at the base of the mixed layer may be described by a one-sided Gaussian curve. K_z is then estimated from the increase of the second moment, the square of the mean width of each profile, with time. This approach is dependent upon the low variability across the patch and little variability in the density profile. The propagation of internal waves causes variation in the SF_6 profiles and the tracer distribution is referenced to the average density-depth profile for the survey period to correct for the isopycnal variation. K_z estimates derived from SF_6 tracer distributions vary by almost an order of magnitude. The K_z obtained from the subducted tracer patch during IronEx I was 0.25 $cm^2\ s^{-1}$ at a stable pycnocline (Law *et al*., 1998), whereas it was greater (1.95 $cm^2\ s^{-1}$) at the weaker pycnocline in a North Atlantic anti-cyclonic eddy (Law *et al*., 2000).

The vertical exchange of nutrients and gases may be determined by application of the derived K_z to the gradient at the base of the mixed layer. This approach provides an independent estimate of new production by constraining the transfer of nitrate from deep waters, which can be compared with new production estimates from *in vivo* stable isotope incubations (Law *et al*., 1998). In the Southern Ocean, vertical diffusion represents a source of dissolved iron, and preliminary estimates of K_z from SOIREE suggest that this pathway is more significant than atmospheric input in this region (Bowie *et al*., 2001).

Three-dimensional tracking

IronEx I demonstrated the utility of the SF_6 tracer in that, following subduction beneath a low-salinity front, the iron-enriched patch was still tracked by the tracer signal. Although sampling capability was reduced, as surface mapping was no longer practical and the patch has to be located by vertical profiling, this response to the iron could still be monitored.

Limitations

The SF_6 Lagrangian framework places certain logistical limitations, although these are minor compared with the benefits. Determination of the patch boundaries and identification of the centre dominate the programme and prevent continuous profiling at the patch centre, although this can be resolved by a two-ship exercise. Site selection may be biased by the need to identify a site in which a tracer Lagrangian experiment will be sustained, and so dynamic regions, such as fronts should be avoided. Similarly, surface mixed layers which are too deep, or too shallow, may potentially shorten the lifetime of the tracer patch.

A consideration of SF_6 tracer applications is the infrared activity of the SF_6 molecule, although the volume required for a mesoscale surface release is minimal when compared with total global SF_6 production (2000 tonnes p.a., Ko *et al*., 1993). It is estimated that the total SF_6 for a surface tracer experiment (including that released during saturation) has a radiative forcing equivalent to the CO_2 produced during 1–2 days research ship on passage.

Whereas the contribution of surface releases to the atmospheric signal is negligible, the background SF_6 signal in the ocean may be influenced in the event of subduction. SF_6 has considerable potential as a transient tracer of water mass ventilation and, following the stabilisation of the atmospheric CFC (chlorofluorocarbon) concentrations (Walker *et al.*, 2000), offers an alternative approach for tracking transport of recently-formed water into the deep ocean (Law *et al.*, 1994; Law *et al.*, 2001). However, even if subduction of a surface tracer patch occurs immediately after release, the impact of an additional 50–120 g upon sub-thermocline tracer concentrations will be minor, following dilution.

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Prediction of the physical behavior of released iron by random walk simulation during the iron fertilization experiment in the North Pacific

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At an iron fertilization experiment, it is important to predict the behavior of released iron in the surface water. Its behavior is complex because both physical and biogeochemical processes are involved. Simulations of a sulfur hexafluoride (SF_6) tracer release experiment is useful for understanding the physical behavior of released iron. The behavior of SF_6 is controlled by only physical processes.

A random walk simulation was employed to predict the physical behavior of released SF_6 in seawater. The random walk simulation is one of a number of particle tracking methods. Particles move by advection and diffusion in a random walk simulation. Stratification, oceanic currents and a diffusion coefficient were the physical conditions considered in this simulation. These conditions were set by typical values observed in the northwest and northeast Pacific. The influence of initial patterns of released SF_6 on the behavior of iron was also considered in the simulation in order to find an efficient release pattern of iron and SF_6. Time scales of this study were 4–5 days, 2 weeks and 1 month. This simulation acquired spatial scales that depend on time scales. As a result of this simulation, we would like to propose items of observation for simultaneous SF_6 tracer release experiments. We also performed a random walk simulation on the ocean general circulation model in the North Pacific. We found that the water mass moved from the northwest Pacific to the northeast Pacific by advection over several years. It suggests that the release of large amounts of iron and SF_6 in the northwest Pacific affects conditions in the northeast Pacific in several years.

Influence of Cape St. James on currents and eddies in the Gulf of Alaska

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Cape St. James lies at the southern tip of the Queen Charlotte Islands off the West Coast of British Columbia. The swift tidal streams and strong prevailing outflow currents at this cape contribute to the Haida Eddies in the Gulf of Alaska, and to outflow jets and plumes in the neighboring coastal waters. The waters at the cape itself are rich in marine life, and nutrients including iron, due to outflow of coastal water, and intense tidal mixing that stirs deep nutrient-rich water to the surface. Thomson and Wilson (1987) described an anti-cyclonic eddy that forms to the southwest of this cape, due to tidally rectified outflow currents. Crawford *et al.* (1995) found that wind-forced currents enhanced this outflow, especially in winter when storms are most intense and frequent. Satellite altimetry and infrared temperature observations provide additional insight into this region. We have re-processed the TOPEX/ Poseidon (T/P) and ERS-2 altimetry data using tidal constants based on regional tidal models (Foreman *et al.*, 2000), and on T/P data themselves (Cherniawsky *et al*., 2001.) We have also searched through 10 years of AVHRR measurements from NOAA satellites. In winter, the eddies that form to the southwest of Cape St. James often advect northward along the West Coast of the Queen Charlotte Islands with the prevailing winter coastal current. These anticyclonic eddies eventually separate from shore, forming the Haida Eddies, which can drift for several years in the Gulf of Alaska. Normally one or two such eddies form every winter, with larger eddies forming in major El Niño winters. We also find that Haida Eddies may originate along the Northwest Coast of the Queen Charlotte Islands, far from Cape St. James, supporting the hypothesis that local baroclinic instability of coastal currents is another generating mechanism for this class of eddies.

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APPENDIX 2

Terms of Reference for the Advisory Panel on *Iron fertilization experiment in the subarctic Pacific Ocean*

The original Terms of Reference (items 1 to 3 below) were approved at the PICES Eighth Annual Meeting (October 1999, Vladivostok, Russia). The Terms of Reference were expanded to include item 4, below, at the PICES Thirteenth Annual Meeting (October 2004, Honolulu, U.S.A.).

1. Examine the reasoning for a subarctic iron enhancement experiment;

2. Examine the scale, disciplines, and resources (personnel and ships) required ensuring success of the experiment;

3. Design the experiment and its timing, particularly, the suite of chemical measurements and forms of iron, the biological parameters, the tracking of the spread of iron-induced bloom using SF_6 tracer

4. To synthesize, compare and contrast the results of conducted experiments (SEEDS-I & II and SERIES), and to develop new experimental strategies and hypotheses to explain the different biogeochemical responses to iron enrichment.

APPENDIX 3

Historical List of Advisory Panel Members on *Iron fertilization experiment in the subarctic Pacific Ocean*

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APPENDIX 4

IFEP-AP Annual Reports

1999 Report of the Advisory Panel on *Iron Fertilization Experiment in the Subarctic Pacific Ocean*

(PICES Eighth Annual Meeting, October 8–17, 1999, Vladivostok, Russia)

The Advisory Panel on "An Iron Fertilization Experiment in the Subarctic Pacific Ocean" (IFEP) met on October 14. The IFEP Co-Chairman, Dr. Shigenobu Takeda, welcomed the members of the Panel and observers and called the meeting to order. The agenda was reviewed and accepted without changes.

Drs. Takeda and Paul J. Harrison introduced the IFEP objectives reflected in the terms of reference. Iron fertilization of HNLC (High Nutrients Low Chlorophyll) water is one possible approach to remove CO_2 from the atmosphere to combat global warming caused by GHGs. Natural iron fertilization has been hypothesized to control glacial/interglacial shift in atmospheric CO_2. Iron fertilization experiments were repeatedly done in the equatorial Pacific under the IronEx Programs I and II, and recently in the Southern Ocean. The Subarctic Pacific, with different biology and unique water structure (*e.g.*, strong pycnocline, fresher mixed layer) from the other two regions, is the only HNLC region without such an experiment to assess the CO_2 removal question related to iron. The Panel will (i) examine the reasoning for a subarctic iron experiment, the scale disciplines, and resources required to ensure success of the experiment, and (ii) design the experiment and its timing.

Drs. William Cochlan and Mark L. Wells gave a brief overview of IronEx I and IronEx II. In particular, Dr. Wells pointed out the importance of understanding the iron chemistry: What happens to the iron when it is added? Does it precipitate out?

Dr. Harrison presented physical, chemical and biological conditions at Station P, a potential site for the iron fertilization experiment in the eastern North Pacific. He also discussed eddies forming off the Queen Charlotte Islands in winter and whether whey could be used as an iron fertilization site. Dr. Josef Cherniawsky provided more details on the physics of the eddies. The IFEP members agreed that additional information is required to decide if these eddies would be a suitable fertilization site, an alternative to Station P.

Dr. Wells suggested that questions be formulated in order to test specific hypothesis and then decide on needs for the measurements and personnel. The following questions were drafted:

- What are the driving hypotheses for a fertilization experiment? Is it industry driven or science driven?
- What are the motivating questions and what are the best ways to answer these questions?
- How is a fertilization experiment going to improve our understanding of the iron response and what aspects of the response do you want to examine?
- What will a fertilization experiment tell you that the bottle enrichment experiments and mesocosm experiments have not?
- Why conduct an experiment at Ocean Station PAPA and the northwest subarctic Pacific?
- What will it tell you that SOIREE, SOFeX, Caruso and IronEx have not told you?

The Panel discussed the analytical resources needed to be brought to bear on the problem. A list was created in which all recommended measurements were arranged into two groups, primary and secondary importance. The IFEP members from each country were requested to announce the experiment to colleagues, distribute the list and ask who would be interested in participating and what they could measure/contribute. A list of suggested participants should be sent to IFEP Co-Chairmen October 2000.

The Panel reviewed a draft workplan developed during 1999 by correspondence. Presently the iron fertilization experiment is planned for August 2002 at Station P in the northeast subarctic Pacific and May or June 2003 at Station KNOT in the northwest subarctic Pacific. There is a chance for a preliminary experiment in spring 2001 in the northwest subarctic Pacific. The Panel recommends to convene a 2-day planning

workshop on “Designing the iron fertilization experiment in the Subarctic Pacific” (co-sponsored by PICES and CRIEPI), prior to the PICES Ninth Annual Meeting. Co-Convenors are Drs. Shigenobu Takeda (Japan) and C.S. Wong (Canada). The objective of the workshop is to initiate planning for experiment, including logistics and funding, *etc*. IFEP requests that PICES provide funds for three invited speakers to attend the workshop.

2000 Report of the Advisory Panel on *Iron Fertilization Experiment in the Subarctic Pacific Ocean*

(PICES Ninth Annual Meeting, October 20–28, 2000, Hakodate, Japan)

The Advisory Panel on An Iron Fertilization Experiment in the Subarctic Pacific Ocean (IFEP) met in the evening of October 25. The Co-Chairman, Dr. Shigenobu Takeda, welcomed the members of the Panel and observers (*IFEP Endnote 1*) and called the meeting to order. The agenda was reviewed and accepted without changes.

A 2-day IFEP Planning Workshop on "Designing the iron fertilization experiment in the subarctic Pacific" was convened in Tsukuba, Japan, prior to the PICES Ninth Annual Meeting (October 19-20, 2000). A report of the Workshop appears as *IFEP Endnote 2*. The objective of the workshop was to initiate planning for the experiment, including logistics, ships, funding, *etc*. The workshop was very successful thanks to 19 excellent presentations and spirited discussion among 39 participants.

Dr. Takeda introduced the schematic diagram of subarctic plankton ecosystem that includes new biological and geochemical processes reported during the workshop. He also listed similarities and differences in physical, chemical and biological characteristics between the eastern and western subarctic Pacific. Such differences have a close relationship with the zonal gradients in atmospheric iron deposition.

From the results of the workshop, Dr. Paul J. Harrison proposed a central hypothesis for the iron enrichment experiments in the subarctic Pacific. The hypothesis was adopted by IFEP after modification according to the suggestions and comments from Drs. Kenneth Coale and Phillip W. Boyd, and other members (*IFEP Endnote 3*). The experiment should be driven by a scientific hypothesis and is to test the hypothesis on natural ecosystem and geochemical cycles, therefore the word "fertilization" would be replaced by "enrichment".

IFEP recognizes that it is very important to have a close linking between the Canadian and Japanese program. It is considered that scientists and ships from both Canada and Japan should perform the eastern and western experiments as a collaborative program to make the east-west comparison stronger by using the same methodology and team. The experiment needs the participation of American scientists and ships as well as scientists from other PICES countries to maintain the international activity achieved during the workshop. Due to the number of scientists that is needed to measure a wide variety of parameters, the experiment will require more than two ships. The R/V *J.P. Tully* (Fisheries and Ocean Canada) and R/V *Kaiyo-Maru* (Fisheries Agency, Japan) or T/S *Oshoro-Maru* (Hokkaido University, Japan) will be the base ships, both in the eastern subarctic experiment in July/Aug 2002 (Station P) and in the western subarctic experiment in August 2003 (45–50°N, 160–165°E). The R/V *Hakuho-Maru* (University of Tokyo, Japan) is also available to perform the survey for studying the long-term responses in October 2003. A preliminary experiment in the western subarctic in June–August 2001 is also planning to use the R/V *Kaiyo-Maru*.

The Panel discussed the timeline of proposals for research and ship time. The IFEP members from each country were asked to gather information such as what they could measure/contribute to prepare the proposals as an international program. The information will be distributed to colleagues who are interested in participating.

IFEP recommends using a web site on the PICES home page to improve communication between IFEP members and other scientists (group of American scientists) who are proposing to participate in the Canada-Japan experiments.

After the successful IFEP planning workshop, the IFEP felt strongly that the next step should be to convene a half-day mini-workshop or meeting at the PICES Tenth Annual Meeting in Victoria. This workshop would refine the details of the experimental design for 2002 and 2003 with information about a preliminary experiment in the western subarctic gyre in 2001 and Southern Ocean experiments in 2000–2001.

IFEP Endnote 1

Participation List

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Lev M. Gramm-Osipov (Russia)
Paul J. Harrison (Canada)
Isao Kudo (Japan)
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Philip W. Boyd (UK)
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IFEP Endnote 2

Report on IFEP Planning Workshop on Designing the Iron Fertilization Experiment in the Subarctic Pacific

Venue: Tsukuba, Japan, October 19–20, 2000
Conveners: C.S. Wong and Shigenobu Takeda
Co-Sponsors: PICES and the Japan Central Research Institute of Electric Power Industry (CRIEPI)

Objectives of the workshop

a. To establish the current knowledge about the role of iron in limiting phytoplankton production in the subarctic Pacific;
b. To identify the specific questions that should be answered by the *in situ* iron fertilization experiment in the subarctic Pacific; and
c. To initiate planning for the experiment, including logistics and funding, etc.

Scientific Sessions

1. *General overview of IronEx and SOIREE, iron chemistry and biology in seawater*
2. *Physics in the North Pacific and Fe addition techniques*
3. *Biology in the North Pacific and IronEx*
4. *Chemistry in the North Pacific and IronEx*

The workshop was very successful thanks to 19 excellent presentations and the spirited discussion from the 39 participants.

What do we know from IronEx I and IronEx II and SOIREE, *etc*.?

- Iron limitation is clearly present in populations of phytoplankton in HNLC regions.
- Iron enrichment de-couples larger phytoplankton from the meso-zooplankton community.
- Evidence for carbon export in SOIREE is not clear. There may have been export of carbon, yet retention of iron. Evidence for carbon export in IronEx is clearer.
- Response in SOIREE was much slower than the response in IronEx.
- There is now more interest in the effect of iron enrichment in different macro-nutrient-limited regimes, specifically in low NO_3 regimes where N-fixation dominates N-uptake.
- A ship-based study of light limitation of iron enrichment in the SOIREE region showed that light limitation is present at 100 m.
- There is some interest in long-term addition experiments of low levels of iron.
- The role of meso-scale eddies is intriguing at Station P. They may offer a way to track a patch of water for years, but the phytoplankton community in an eddy may be atypical of the Gulf of Alaska. Eddies also have no surface water expression and so their relevance to an iron enrichment experiment is not clear.

- The European community has just sent the *Polarstern* to the southern ocean (in the Atlantic sector) to do a SOIREE-type experiment over a longer time (CARUSO).

What do we still need to know?

- There is a need to study Station P and the NW Pacific, but other regions need to be studied as well.
- The fate of primary production (carbon): POC export flux, DOC, respiration and response of higher trophic levels (is there an increase in fish production?). The time scale is over a year, so the model approach is needed).
- What are the roles of ligands? What members of the community produce and take up ligands?
- Does zinc affect other enzyme processes?
- Need DMS/DMSP studies and other climate change biogases. Previous iron enrichment studies have measured DMS production. Should have both ships and aircraft for sampling. At Station P, ocean levels of DMS are very high and atmospheric levels are low.
- Need to know the factors that influence the carbon-to-nutrient and other trace metal export ratios.
- Iron might end up below the mixed layer during long-term commercial projects. It might become available the next summer after winter mixing.
- Would long-term iron enrichment drive a system toward another limitation (N, Si, Zn, Co, *etc*.)?
- What is the impact of long-term iron enrichment on fish? Governments may see the fish production as a secondary benefit of the iron enrichment, so this question will be asked. The public may see this as a problem, due to "wrong" species benefiting, such as pennate diatoms that produce domoic acid. (These are not questions that can be addressed with the current experiment.)
- What are the chemical processes associated with iron saturation and super-saturation of seawater?
- How does Fe(II) stay around so long in Fe enrichment patches?
- What are the major grazers on diatoms and how do they respond when diatom (pennate/centric) abundance increases?
- Understanding the dynamics of plankton ecosystem, export carbon flux and climate related gases to the iron enrichment is appropriate for the requests of Government and Industry who are seeking scientific information to asses the effect on future global atmospheric CO_2 and environmental impacts.

What do we hope to learn from an iron enrichment experiment at Station P and WSG?

What are the similarities and differences in the plankton ecosystem response to iron fertilization in the subarctic Pacific? There is a special interest in the east-west North Pacific comparison, which includes differences in dominant species (pennate/centric diatoms) and export flux (Org-C/Opal/$CaCO_3$).

Canadian program (extracted from the Canadian SOLAS proposal)

Canadian scientists are proposing to fertilize a 64 km^2 patch of ocean near Stn P in the NE subarctic Pacific during July/Aug 2002. Iron will be added 3 or 4 times during the three week experiment and a wide variety of physical, chemical and biological parameters will be measured. In particular, the expected increase in phytoplankton biomass and the subsequent carbon flux out of the photic zone, the drawdown in CO_2, and the production of other climate change gases such as DMS will be carefully documented.

There are several reasons why an iron enrichment experiment should be conducted at Stn P in the NE subarctic Pacific. Station P or Ocean Station Papa (50°N 145°W) has a 40-year time series of physical, chemical, and biological parameters and thus it has one of the longest open ocean time series in the world. Three large intensive sampling programs have provided detailed information, especially on biological rate process studies (SUPER, WOCE, and Canadian JGOFS). This large published data set/time series will provide an excellent background to assess the annual and interannual natural variability for evaluating the magnitude of the response to the

iron addition experiment. The subarctic North Pacific represents a latitudinal gradient between the polar (Southern Ocean) and equatorial regions and therefore an iron addition experiment at Station P will allow a comparison among the three large HNLC regions and between the eastern and western gyres in the subarctic Pacific.

The subarctic NE Pacific has different physical, chemical and biological properties than the other two HNLC regions (Southern Ocean and Equatorial Pacific). In particular, it has a very shallow summer mixed layer depth, a strong, shallow pycnocline and low currents which should help to keep the iron patch intact and ensure the success of the experiment. The biodiversity of the plankton is different from the equatorial Pacific and Southern Ocean and therefore the response to the iron addition and the flux of carbon out of the photic zone may be different.

Unlike the equatorial Pacific, Station P is in close proximity (3 days) to major research laboratories at the Institute of Ocean Sciences and the University of British Columbia and therefore it should be easier to document the longer term recovery from the iron addition. If the detailed documentation of the ecosystem response to a singe iron addition is successful, this will allow us to proceed to the next phase, repeated iron additions and the longer term monitoring that this will require.

Key questions that have not been entirely resolved by previous iron enrichment experiments, are:

1. How does the change in biodiversity and foodweb structure differ for markedly different ecosystems which have been perturbed by an iron addition?
2. What is the drawdown of CO_2 and especially the flux of carbon to the deep ocean?
3. How does the production of ligands influence the iron chemistry and the longevity of the phytoplankton bloom?
4. How does zooplankton grazing influence the formation of the bloom and the carbon flux (*e.g.*, fecal pellet production)?
5. What is the long-term response and recovery of the ecosystem following an iron addition?
6. What is the magnitude of production of other climate change gases such as DMS during the bloom and how is the production influenced by phytoplankton species, microbial processes and grazing?

Objectives

1. To measure the response of bacteria, phytoplankton and zooplankton in terms of species, standing stocks and rate processes to the iron addition.
2. To measure the drawdown of CO_2 and the flux of carbon to depth.
3. To study the relationship between ligand production and the associated changes in the iron chemistry and their influence on the longevity of the phytoplankton bloom.
4. To assess the influence of zooplankton grazing on the phytoplankton bloom formation and carbon flux.
5. To follow the long-term response and recovery of the phytoplankton bloom.
6. To quantify the production of various climate change gases during the iron enrichment experiment and assess the factors which influence the production of these biogases.

Biological oceanographic sampling

The upper 150 m will be sampled vertically (6–8 depths) each day using 12 acid-cleaned PVC samplers on a CTD/water sampler rosette system at the patch center (determined by SF_6 levels) and in the surrounding waters. Real-time vertical profiling of temperature, salinity, transmissivity, chlorophyll *a* fluorescence and underwater irradiance (PAR, 400–700 nm) will be carried out. Discrete water samples will be analysed for:

- chlorophyll *a* (size-fractionated, >20, 5–20, 2–5 and 0.2–2 µm)
- heterotrophic bacterial abundance
- microzooplankton abundance
- phytoplankton abundance (flow cytometry, epifluorescence and light microscopy).

Additional samples will be incubated on deck to measure rates of:

- primary production (14°C, 24 h incubation, simulated *in situ* and size-fractionated as for Chl-*a*)
- bacterial production
- microzooplankton grazing

Mesozooplankton abundance will be assessed from 150–0 m vertical hauls. The Th:U activity ratio of particles in the upper water column will

be collected using a submersible pumping system.

Geochemical measurements

Two types of sampling will be done: hydrocasts and underway sampling from the vessel's non-toxic seawater supply (intake 5 m subsurface) and analysed by fluorometry (calibrated with discrete chlorophyll *a* samples every two days, corrected for quenching during daylight hours), and using a bubble-segmented automated nutrient analysis system, respectively. Underway samples for dissolved iron will be conducted from a clean towed batfish sampling system, and samples for pCO_2 will be drawn from the vessel's non-toxic seawater system. Phytoplankton samples for the single-cell flavodoxin assay will be pre-concentrated onboard ship and later analysed shoreside. Sampling will be conducted by:

- Towed batfish: Continuous sampling will be made from a towed batfish with a clean pump and tubing for the following measurements (This is not a pumping undulating fish):
  - Conductivity/salinity sensor
  - SF_6
  - fCO_2, pH
  - nitrate
  - iron
  - chlorophyll *a* (fluorometer)

- Hydrocasts by rosette CTD/Niskin samplers:
  - T, S
  - O_2
  - Chlorophyll *a*
  - Macro-nutrients (N, P, Si) by auto-analyzer
  - Iron by chemiluminescence
  - Particulate iron size-fractions, total iron, dissolved iron
  - SF_6
  - DIC, TA, pH
  - DOC, DON, POC
  - DMS

- Free-drifting sediment traps (at 50 m intervals, 50–600 m) deployed and retrieved at 3 day intervals to obtain samples for detritus organic C, N, P, Si, PIC, Fe, Cd, Al, rare earth elements, Th/U ratios, coccolithophore counts, and planktonic species, and scanning electron microscope pictures.

- Deckboard perturbation experiments: Algal carbon, growth rates and C:Chl-*a* ratios, *etc*.

Drs. Wong and Harrison hope to have one or two strings of moored sediment traps, plus free floating traps. Moored traps would be at the control site. Floating traps would hopefully follow the patch. It will be difficult to keep the patch and traps together, but there is a real need for trap data to try to quantify and characterize export. Free-floating sediment traps may perform differently than moored traps. Therefore we should have free-floating traps in and out of the Fe patch.

There is a need to know more about micro-zooplankton and to know the effects of ligands and climate change biogases (including but not limited to DMS, CO_2, N_2O). SOIREE showed enhancement of nitrous oxide at the top of the thermocline. There will be aircraft-based sampling of gases and aerosols above the Fe patch. The experiment expects to have access to the R/V *J.P. Tully* for 4 weeks, but anticipates sampling over a longer time if back-to-back cruises using a second vessel can extend sampling over 6 weeks. Cruises could be separated by several weeks if the patch could be found on the second cruise. Iron limitation at Station P in July to August is severe, so the project will be conducted during this period. The project will be part of the Canadian SOLAS project.

Summary of Japanese programs

Japanese scientists are proposing to conduct a preliminary experiment of about 40 days duration in June–August 2001, using the R/V *Kaiyo-Maru* in the Western Subarctic Gyre. The next effort is anticipated for August to mid-September 2003 using either the R/V *Oshoro-Maru* or the R/V *Kaiyo-Maru* to initiate the SF_6/Fe patch and conduct the basic study. In October 2003, the R/V *Hakuho Maru w*ill be used for intensive sampling and measurements and assessing long-term responses. Sampling will occur in the Western Subarctic Gyre in the region 45–50°N, 160–165°E:

1. To measure the response of bacteria, phytoplankton and zooplankton in terms of species, standing stocks and rate processes to

the iron addition;
2. To measure the drawdown of CO_2 and the flux of carbon export;
3. To study the interaction between biogeochemical processes in the surface water during the phytoplankton bloom and the production of climate gases in the atmosphere;
4. To study the relationship between phytoplankton (diatom) production and the higher trophic level (salmon); and
5. To assess the influence of iron supply on the characteristics of the plankton ecosystem in the western subarctic Pacific.

The proposal would be funded by:

- The Science and Technology Agency (2001–2005);
- Ministry of Education, Science and Culture (2001 Basic Science, 2002–2004 Scientific project with high priority);
- NEDO grant.

Japan SOLAS is still in the preparation stage. A study of the influence of natural atmospheric iron supply on the characteristics of the plankton ecosystem in the western subarctic Pacific will be one of the important topics. (Long cruise staying at a station in the high dust season in spring.)

United States, SOFEX (by Kenneth Coale)

- Experiment will be along 170° west, near SO-JGOFS site.
- Experiment will use SeaSoar type of device that pumps water to ship.
- SO-JGOFS found a jump in silicate at Polar front near 62°S, with increase south of front. SOFEX will do experiments N and S of front, to see which type of species is enhanced in each region (*Phaeocystis* and diatoms).
- Big complement of scientists and studies. There are ten more scientists than berths on ship. Lack of ship bunks is a general problem in iron enrichment cruises. For example, samples will be frozen for later analysis by Edie Rue and will run the only ligand study.
- SOFEX will need to find the northern patch after a week or more, and plan to use Lagrangian drifters to keep track of the patch.

Methodology

- Need to standardize sampling methods to enable comparison among experiments in different HNLC regions. List of dominant species and their biomass is useful for the comparison. Export production is difficult to get quantitative samples?
- First step is the application of previous IronEx methodology ($FeSO_4$, initial concentration level, Fe infusion timing, *etc*.) and then we may go to new method such as the use of chelated iron (iron lignite), long-period and low-level iron supply, *etc*.
- Should add DMSP to list of samples.
- Micro-zooplankton are important grazers and dilution experiments are necessary to quantify coupling of primary production and grazing.
- Fe organic ligand study has technical problems.
- Analyses of biogases in the atmosphere are important, but how?
- Bag experiments have limitations. Small bags might not represent the ocean. Large bags are too difficult to manage. However, there should be some role for bag experiments.
- Use of organic chelated iron (iron lignite) may provide carbon source for hetero-trophic organisms.
- Stable isotope study will be done in SOFEX to see the proxy of paleo-oceanographic environment.
- After silicate in surface water will be used up, a re-infusion of Fe will give us some idea of the long-term change in dominant species.

Logistics issues

- The Station P project needs a second ship. Kenneth Coale recommended that a U.S. ship may be available if a group of American scientists were to propose to participate. The U.S. SOLAS program would be one way to generate support. It would help to have a Canadian–Japanese proposal ready. U.S. scientists must start to prepare proposals now for Station P 2002 cruise.
- A Canadian or U.S. airplane would be useful for tracking the Fe patch. An airplane with a hyperspectral sensor would be really useful.
- ADEOS-2 will be launched soon. It will be useful (similar to SEAWIFS).

IFEP Endnote 3

Proposed experimental summary

The North Pacific is characterized by relatively uniform distributions in temperature, salinity, macronutrients and light yet strong zonal gradients in atmospheric iron deposition exist between the eastern and western gyres.

We hypothesize that:

1. The difference in episodic iron deposition gives rise to distinct phytoplankton communities that characterize these biogeochemical provinces.
2. The biogeochemical response of any given province (air–sea flux of biogases, export flux of carbon) is driven by episodic events such as iron deposition.

To test these hypotheses (and offers as part of this program) an iron perturbation experiment, on the scale of the entire community is required such that the community response and resultant geochemical signal can be measured.

Scientific questions

- What is the fate/longevity of the bloom with an emphasis on ligand production and the response of the grazers (micro and mesozooplankton)?
- What is the magnitude and characteristics of particles (Carbon flux) sinking at the end of the bloom?
- What is the production of various climate change biogases (DMS, N_2O, methane, *etc*.) during and after the bloom?

2001 Report of the Advisory Panel on *Iron Fertilization Experiment in the Subarctic Pacific Ocean*

(PICES Tenth Annual Meeting, October 5–13, 2001, Victoria, Canada)

The meeting was held from 08:30–17:30 hours on October 6, 2001. The Co-Chairman, Dr. C.S. Wong, called the meeting to order and welcomed the participants (*IFEP Endnote 1*). The Advisory Panel reviewed the draft agenda and it was adopted (*IFEP Endnote 2*). The meeting focused mainly on the results of the successful Japanese iron enrichment experiment in July 2001, and planning for the Canadian SOLAS iron enrichment experiment to take place at Station P in July 2002.

Summary of Japanese iron enrichment experiment in the western subarctic Pacific

A preliminary iron enrichment experiment was conducted during the FRV *Kaiyo-Maru* cruise in June–August 2001. The next larger scale experiment in the western gyre is planned for August–September 2003.

Five goals of the overall project were:

1. to measure the response of bacteria, phytoplankton, and zooplankton in terms of species, standing stocks and rate processes to the iron addition;
2. to measure the draw-down of CO_2 and the carbon export flux;
3. to study the interaction between biogeochemical processes in the surface water during the phytoplankton bloom and the production of climate gases in the atmosphere;
4. to study the relationship between phytoplankton (diatom) production and the higher trophic level (salmon); and
5. to assess the influence of atmospheric iron supply on the characteristics of the plankton ecosystem in the western subarctic Pacific.

This first iron enrichment experiment was rather rushed since funding was received in February 2001, the ship allocated in April, and the experiment conducted in June. It included only 16 scientists. The experiment provided the most dramatic phytoplankton response of any of the HNLC iron enrichment experiments done to date.

Overview of the Subarctic Pacific Iron Experiment for Ecosystem Dynamics Study (SEEDS 2001)

Experiment

An *in situ* iron enrichment experiment was conducted in the western subarctic gyre of the North Pacific (48.5°N, 165°E) from July 18 to August 1, 2001. The experiment consisted of a single addition of 350 kg of iron as $FeSO_4$ with an inert tracer gas SF_6, over an 8×10 km patch with a mixed layer depth of 10 m. The iron release track was up and down along a north/south line generating a radiator pattern relative to the central buoy due to surface currents. The injection was completed on July 19, and followed by two weeks of observations. The patch moved ~ 100 km from the beginning to the end. Drogues were used to follow the patch for ~ 24–48 h, and were repositioned every two days.

Iron

Prior to release, dissolved iron concentrations in the ambient surface seawater were extremely low (<0.05 nM). At the first underway transect throughout the patch after the iron release, significant increase of dissolved iron (1.9 nM, mean value calculated using all measurements of first underway transect in the patch; maximum 6.0 nM) was observed, and most of dissolved iron was in the colloidal fraction in the mixed layer. Dissolved iron concentrations subsequently decreased rapidly, and the loss rate gradually decreased. High particulate iron concentrations (>1 nM) were observed throughout the experiment.

Biological responses

The first biological response to the iron enrichment was the increase in photochemical quantum efficiency (F_v/F_m) of phytoplankton on day-3 from the enrichment. Chlorophyll *a* increased from day-6 and reached 20 mg m^{-3} on day-10. The maximum differences between outside and inside the patch were 19.5 mg m^{-3} in chlorophyll *a*, and 11.7 μM in nitrate. Dominant phytoplankton species before the fertilization and

outside the patch was the pennate diatom *Pseudoniztschia pungens*. But in the patch, phytoplankton rapidly increased and large-sized (>10 μm) centric diatoms, mainly *Chaetoceros debilis*, were observed. Non-depletion in nitrate until the end of the observation, and shallower euphotic layer depth than the mixed layer observed on day-12, suggested that phytoplankton was light-stressed at the end of the experiment. Salmon and small squid abundance, collected by trawl sampling, were not changed between inside and outside of the patch, but northern mackerels were abundantly collected only in the patch.

pCO_2

The underway pCO_2 system with high measurement frequency (1-minute interval data logging) with real-time monitor facilitated tracing the enrichment patch with biological draw-down of pCO_2. The pre-experiment condition of the iron enriched area showed uniform pCO_2. The change of pCO_2 inside the patch was observed after 5 days of the iron enrichment. The draw down of pCO_2 expanded up to 146 μatm after 11 days of the enrichment.

Export flux

Export flux was measured using drifting sediment traps (Knauer type). The depths of the traps were 20, 40, 60, 100 and 200 m from the sea surface. The trap inside the patch was applied and recovered at about 2-day intervals. The reference trap outside the patch was applied and recovered at about 4-day intervals. The majority of the trapped material was fecal pellets of zooplankton. Increase of export flux was observed after 7 days of the enrichment. Wind-driven deviation of the inside-patch trap occasionally occurred, which made it difficult to estimate the export flux accurately, however, the increasing export flux inside the trap was apparent. Longer observation of the iron-enriched patch is needed to see the fate of accumulated organic carbon after the end of diatom blooming.

Bottle incubation experiments

Bottle incubation experiments on board were also conducted to elucidate the effects of iron concentration and temperature on the growth of phytoplankton and nutrient utilization. Subsurface seawater samples taken on day-2 were spiked with $FeCl_3$ ranging from 0 to 2 nM, and incubated at 5, 9, 13 and 18°C for 14 days. The bottle incubation revealed that the increase in chlorophyll *a* was almost the same between *in situ* and *in vitro*, but the draw-down of nutrients was much faster *in vitro* than *in situ*. The specific growth rate increased with the amount of spiked $FeCl_3$, and was also the function of incubation temperatures.

Planning session for Canadian SOLAS iron enrichment experiment in July 2002

Key issues to focus on in this experiment are:

1. What is the influence of Fe enrichment on the production of climate active gases? This is the central novelty of the Canadian SOLAS iron enrichment project.
2. What is the fate of carbon and carbon export? This question is also central to SOLAS because of CO_2 flux, and it is of general interest because of poorly restrained export in previous iron enrichment experiments.
3. What is the plankton community's (ecosystem) response to iron enrichment?
4. What happens with iron chemistry, ligand production, and fate of iron?

Discussions centered on technical preparations such as iron and SF_6 tanks, drogues, iron injection and following the patch.

Overview of NSF proposal

Scientists from the U.S.A. would like to take part in both the east and western gyre iron enrichment experiments. The highlights of the proposal submitted to NSF are as follows:

- Characterize the community and water chemistry within and adjacent to the iron-enriched patch over a time period of several weeks (20–50 days) after the initial enrichment;
- Test a series of sub-hypothesis using on-deck incubation studies;
- Assess the phenotypic differences of newly-isolated dominant subarctic Pacific diatoms in laboratory culture experiments; and
- Model the planktonic response to changes in iron concentrations and chemical speciation

in the iron-enriched patch over a time period of several weeks after the initial fertilization.

Should we establish a SOLAS component of PICES?

Discussions focused on a proposal for an iron working group since the iron work was underway, and would benefit from a North Pacific coordinated effort leading to conclusive results and inter-gyre comparisons in the next three years. The idea of an iron working group was presented to the CCCC Implementation Panel, but it was not put forward to the Science Board.

IFEP Endnote 1

Participation List

Members:

Robert Bidigare (U.S.A.)
William Cochlan (U.S.A.)
Paul J. Harrison (Canada)
Isao Kudo (Japan)
Vladimir Shulkin (Russia)
Atsushi Tsuda (Japan)
Shigenobu Takeda (Japan, Co-Chairman)
Mark Wells (U.S.A.)
C.S. Wong (Canada, Co-Chairman)

Observers:

Melissa Chierici (Canada)
John F. Dower (Canada)
Agneta Fransson (Canada)
Keith Johnson (Canada)
Andrew Leising (U.S.A.)
Maurice Levasseur (Canada)
Patricia Livingston (U.S.A., SB Chairman)
Adrian Marchetti (Canada)
Yukihiro Nojiri (Japan)
Wendy Richardson (Canada)
Hiroaki Saito (Japan)
Nelson D. Sherry (Canada)
Nes Sutherland (Canada)
Charles Trick (Canada)
Frank Whitney (Canada)
Emmy Wong (Canada)

IFEP Endnote 2

IFEP Meeting Agenda

1. Round-table introduction of attendees
2. Adoption of agenda
3. Adoption of first Panel Report of IFEP held in Tsukuba, Japan
4. Review of relevant background work, *e.g.*, eddy transport of iron
   - Where is HNLC water? ENSO factor
   - Iron distribution and possible transport to HNLC waters
   - CO_2 uptake/Fe enrichment in an eddy
5. Review of time-table of international Iron Enhancement Experiments in the subarctic Pacific
6. Review of July Canadian SOLAS iron enrichment planning meeting
7. Summary of Japanese Iron Enrichment Experiment results (SEEDS 2001)
8. SOLAS preparations at IOS
9. Overview of NSF proposal by Wells *et al.*
10. Should we establish a SOLAS component of PICES?
11. Planning session for the Canadian Fe enrichment in July 2002

2002 Report of the Advisory Panel on *Iron Fertilization Experiment in the Subarctic Pacific Ocean*

(PICES Eleventh Annual Meeting, October 18–26, 2002, Qingdao, China)

The meeting was held from 08:30–17:30 hours on October 19, 2002. Co-Chairman Dr. Shigenobu Takeda called the meeting to order and welcomed the participants (*IFEP Endnote 1*). The Advisory Panel reviewed the draft agenda and it was adopted (*IFEP Endnote 2*). The meeting focused mainly on the preliminary results of the successful iron enrichment experiment in the eastern subarctic Pacific in July–August 2002.

Activities in 2002

Eastern subarctic Pacific

An *in situ* iron enrichment experiment in the eastern subarctic Pacific, SERIES (**S**ubarctic **E**cosystem **R**esponse to **I**ron **E**nrichment **S**tudy), was conducted in July–August 2002, as a part of the Canadian-SOLAS project.

SERIES scientific objectives

- Community response to iron addition (comparison with other HNLC regions such as Eq Pacific, S Ocean, NW Pacific);
- Natural longitudinal dust/Fe gradient from Western Subarctic Gyre to Alaska Gyre;
- Fe chemistry and complexing agents;
- Carbon export – needs > 30 days to see;
- Trace gas production *e.g.*, DMS and organic halides.

SERIES implementation - three ships

- CSS *John P. Tully* (Canada): pre-injection survey, patch mapping, buoy handling, underway sampling, nutrients, sediment traps;
- M/V *El Puma* (Mexico, chartered by Canada): atmospheric and ocean process studies (gas production, DMS, DMSP, grazing, BP, PP, Chl, zooplankton, *etc.*);
- M/V *Kaiyo Maru* (Japan): mapping, pCO_2, sediment traps, nutrients, BP, PP, Chl, foodwebs, taxonomy.

Experiment and preliminary results

An *in situ* iron enrichment experiment was conducted in the northeast subarctic Pacific near Station P26 – Ocean Station Papa (50ºN, 145ºW). Site selection was based on the location of waters with low density, uniform physical characteristics, the predominant direction of the drogued drifter buoys, and matching the HNLC condition. There was evidence of two eddy-like features, southwest and northeast of P26, that was taken into consideration.

The first iron release was performed from 01:05–18:45 hours on July 7, 2002. The SF_6 and iron solutions were mixed and pumped over the side at rate of 5 and 20 liters/min to a depth of about 7 m as maintained by attachment of the outlet to a Hi-Fin fish. The release track was an expanding square covering 4.75 × 4.74 n miles, with a distance between transects of 0.4 n miles. Some of the initial values for reactive and unfiltered iron were in the 4 nM range, while dissolved iron concentration was as high as 2.5 nM. Values declined very quickly over the first few days in the surface mixed layer of 10 m. Winds and rough seas mixed the iron down uniformly to about 30 m on July 13 to 14.

Re-infusion of iron was performed from 14:45 hours on July 16 to 08:00 hours on July 17, 2002. An expanding rectangle was used for the re-infusion with the SF_6 mapping system used to monitor the release. The second smaller injection brought levels up to 0.6–0.7 nM for dissolved Fe in the 3–10 m depth on July 17. By July 22, dissolved iron concentrations were very close to background.

Rapid and small initial responses were observed in phytoplankton. As the experiment progressed, the biological response, such as increases in F_v/F_m, primary productivity and Chl-*a* concentration and decreases in macronutrient concentrations, became apparent. This was also augmented by underway pCO_2.

The phytoplankton bloom peaked physiologically around July 21, primary production peaked on July 24, and Chl-*a* peaked on July 24–26 and reached 8 mg m^{-3}.

Concentration of Chl-*a* then decreased gradually to 1.5 mg m^{-3} on August 4. The most dominant phytoplankton at the Chl-*a* peak were centric diatoms, and many pennate diatoms were also observed. Exhaustion of iron and macronutrients seems to be one of the reasons for the termination of the bloom. Sinking particles gradually increased after July 31.

Western subarctic Pacific

The Panel reviewed the results of the Japanese iron enrichment experiment in the western subarctic Pacific – SEEDS 2001 (**S**ubarctic Pacific Iron **E**xperiment for **E**cosystem **D**ynamics **S**tudy). These results will be published as a special issue of *Progress in Oceanography*. The Panel discussed the plans for the second longer-term (>30 days) experiment in this area in July–August, 2004.

Scientific objectives for SEEDS 2004

- Observe the decline of the diatom bloom and elucidate the fate of fixed carbon;
- Measure additional parameters to see the overall biogeochemical responses to iron enrichment;
- Determine the influence of Fe on trace gas production and aerosol formation;
- Measure gas fluxes from ocean surface to atmosphere.

Scientists from the U.S.A. are planning to take part in the longer-term experiment in the western gyre, and the proposal submitted to NSF was presented.

Proposed activities in 2003

IFEP proposes a 3-day workshop on *In situ iron enrichment experiments in the eastern and western subarctic Pacific*, to be held December 4–6, 2003, at the Institute of Ocean Sciences in Sidney, British Columbia, Canada.

Specific objectives of the workshop are:

- Synthesize results from two *in situ* iron enrichment experiments performed in the eastern and western subarctic Pacific (SEEDS-2001 and SERIES);
- Discuss responses in lower and higher trophic levels, carbon cycles, trace-gas production and ocean–atmosphere flux, and models;
- Determine similarities and differences in biogeochemcal and ecosystem responses to iron addition between the eastern and western subarctic Pacific;
- Identify specific scientific questions for the longer-term experiment in the western subarctic Pacific (SEEDS-2004).

The results of the workshop will be published as a special issue of *Deep-Sea Research II*.

IFEP requests support for three invited speakers (two from New Zealand and one from Mexico) to attend the IFEP Workshop in December 2003 in Sidney, Canada.

It was suggested that IFEP needs to work more closely with MODEL Task Team for the improvement of NEMURO model by adding iron limitation to phytoplankton production using the data from two successful iron enrichment experiments performed in the eastern and western subarctic Pacific. Such a model would be useful to see the long-term ecosystem responses as well as the experimental design of SEEDS 2004.

IFEP Endnote 1

Participation List

Members

William Cochlan (U.S.A.)
Paul J. Harrison (Canada)
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Shigenobu Takeda (Japan, Co-Chairman)
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Hiroaki Saito (Japan)
Daniela Turk (Canada)
Nelson D. Sherry (Canada)
Masahide Wakita (Japan)
Shuichi Watanabe (Japan)
Emmy Wong (Canada)

IFEP Endnote 2

IFEP Meeting Agenda

11. Round-table introduction of attendees
12. Adoption of agenda
13. Adoption of the report of the IFEP Panel meeting held at PICES X (Victoria, Canada)
14. Review of time-table of international iron enhancement experiments in the North Pacific
15. Progress report of the Japanese iron enhancement experiment (SEEDS-2001) activities in the western subarctic Pacific
16. Summary of the Canadian iron enhancement experiment (SERIES) in the eastern subarctic Pacific
    - 6.1 Introduction of SOLAS/SERIES
    - 6.2 Overview of logistics and biological responses
    - 6.3 CSS *J.P. Tully* measurements
      Cruise report, SF_6 mapping, iron, DMS, climate gases, pCO_2, carbon, nutrients, sediment trap, and physics
    - 6.4 M/V *El Puma* measurements
      Cruise report, primary production, Chl-*a*, incubation; DMS(P) biology, and aerosol/atmospheric studies
    - 6.5 M/V *Kaiyo-maru* measurements
      Cruise report, mapping, Chl-*a*, FRRF, iron, incubation experiments, pCO_2, nutrients, sediment trap
17. IFEP related activity in other areas
    - 7.1 Overview of SOFeX
    - 7.2 Modeling results of iron enrichment experiments (IronEx-II)
8. Future IFEP related activity plans in the North Pacific
    - 8.1 SERIES/SOLAS
    - 8.2 SEEDS
    - 8.3 US-NSF proposal for post-fertilization long-term study
9. Discuss plans for 2003
    - 9.1 Discuss need for special Symposium /Workshop(s) of SERIES and SEEDS
    - 9.2 Discuss need for PICES Scientific Report(s) of SERIES and SEEDS
    - 9.3 Requests for travel to future meetings
10. Other new business

2003 Report of the Advisory Panel on *Iron Fertilization Experiment in the Subarctic Pacific Ocean*

(PICES Twelfth Annual Meeting, October 9–18, 2003, Seoul, Republic of Korea)

Activities in 2003

SERIES Workshop

A 4-day SERIES (**S**ubarctic **E**cosystem **R**esponse to **I**ron **E**nrichment **S**tudy) Workshop was held March 9–12, 2003, at the Institute of Ocean Sciences, Sidney, Canada. Observed results from the experiment conducted in July–August 2002, in the Eastern Subarctic Pacific by three research vessels, CSS *John P. Tully* (Canada), M/V *El Puma* (Mexico) and M/V *Kayio-Maru* (Japan) were synthesized. Data exchange, publications, timeline for the next 12 months, *etc*. were discussed.

SEEDS planning meeting

A planning meeting for the 2004 SEEDS (**S**ubarctic Pacific Iron **E**xperiment for **E**cosystem **D**ynamics **S**tudy) experiment in the Western Subarctic Pacific was held April 18, 2003, at the Ocean Research Institute, University of Tokyo, Japan. Objectives of the research projects were presented by both US and Japanese scientists. The ship schedule for US and Japanese research vessels and parameters that will be measured on each vessel were discussed.

Activities in 2004

PICES IFEP Workshop

A 3-day PICES IFEP Workshop on "*In situ* iron enrichment experiments in the Eastern and Western Subarctic Pacific" will be held February 11–13, 2004, at the Institute of Ocean Sciences in Sidney, British Columbia, Canada. (The schedule was changed from December 2003 to February 2004.)

Specific objectives of the workshop are:

- to synthesize results from two recent *in situ* iron enrichment experiments in the Subarctic Pacific (SEEDS-2001 and SERIES-2002);
- to discuss responses in lower and higher trophic levels, carbon cycles, trace-gas production and ocean-atmosphere flux, and models;
- to determine similarity and differences in biogeochemical and ecosystem responses to iron addition between Eastern and Western Subarctic Pacific; and
- to identify specific scientific questions for the longer-term experiment in the Western Subarctic Pacific (SEEDS-2004).

The results of this IFEP workshop will be published as a PICES Scientific Report in 2004.

Travel support from PICES is requested (and approved in 2003) for one scientist from New Zealand to attend the workshop.

Topic Session at ASLO/TOS Conference

A 1.5-day special session on "Response of the upper ocean to mesoscale iron enrichment" will be convened February 17–18, 2004, at the ASLO/TOS Ocean Research Conference in Honolulu, U.S.A. The Session represents a combined effort of the Canadian SOLAS and the PICES IFEP.

SEEDS-2004

The second *in situ* iron enrichment experiment in the Western Subarctic Pacific (SEEDS-2004) will take place in July–August 2004. A Japanese ship will release iron on July 17, 2004, stay at the iron-enriched patch for 10 days, and come back to the site from Day 23 to Day 34. A US research vessel will be at the site from Day 6 to Day 26, which allows us 4–5 days' overlapping at the beginning and the end of the experiment.

Publications

Selected papers from the SEEDS-2002 experiment as well as the experimental design of SEEDS-2004 will be published as a special issue of *Progress in Oceanography*.

2004 Report of the Advisory Panel on *Iron Fertilization Experiment in the Subarctic Pacific Ocean*

(PICES Thirteenth Annual Meeting, October 14–24, 2004, Honolulu, U.S.A.)

The meeting of the Advisory Panel on *Iron fertilization experiment in the subarctic Pacific Ocean* (IFEP-AP) was held from 17:00–19:30 hours on October 19 and 19:00–21:00 hours on October 20, 2004. The Panel Co-Chairman, Dr. Shigenobu Takeda, called the meeting to order and welcomed the participants (*IFEP-AP Endnote 1*). A new member, Dr. Hiroaki Saito, was introduced to the Advisory Panel. The draft agenda for the meeting was reviewed and adopted (*IFEP-AP Endnote 2*).

Activities in 2004 (Agenda Items 3 and 4)

In order to review the results and outstanding questions from iron enrichment experiments, and to discuss plans for the second longer-term experiment in the western subarctic Pacific (SEEDS-II), the PICES-IFEP workshop on "*In-situ* iron enrichment experiments in the eastern and western subarctic Pacific" was held February 11–13, 2004, in Victoria, Canada (workshop convenors: S. Takeda and C.S. Wong). 26 scientists from Canada, Japan and the United States of America, and the PICES Secretariat attended the meeting. The workshop started with 4 synthesis talks on SEEDS-I, SERIES and SOFeX, followed by 14 shorter presentations on the physical behavior of the Fe-enriched patch, biological/physiological responses, food-web dynamics, chemistry of iron, carbon cycle, and model prediction. The results of the workshop have been reported in PICES Press (July 2004, Vol. 12, No. 2), and will be published as a PICES Scientific Report in 2004 or early 2005.

A joint Canadian SOLAS/PICES-IFEP session on "Response of the upper ocean to meso-scale iron enrichment" was convened on February 17–18, during the ASLO/TOS 2004 Ocean Research Conference held in Honolulu, Hawaii (session organizers: M. Levasseur, A. Tsuda, W. Miller, W. Cochlan and R. Rivkin). The call for papers was very well received, resulting in a session composed of 23 oral presentations and 17 posters. As expected, the session was a showcase for the most recent experiment: SERIES. But there was also significant contribution from SEEDS and SOFeX, and some presentations proposed thoughtful inter-comparisons between the various meso-scale experiments. This special session allowed the recognition of the similarities and differences in the responses obtained from various *in situ* experiments. The results of the session have been reported in PICES Press (July 2004, Vol. 12, No. 2).

Progress report of the SEEDS-I data synthesis and publication (Agenda Item 5)

In the summer of 2001, a joint Japan/Canada iron enrichment experiment (**S**ubarctic Pacific Iron **E**xperiment for **E**cosystem **D**ynamic **S**tudy – SEEDS-I) was performed in the western subarctic Pacific. A synthesis paper on the experiment was published in *Science* (Tsuda *et al*. "A meso-scale iron enrichment in the western subarctic Pacific induced a large centric diatom bloom", Vol. 300: 958–961, 2003). Twelve manuscripts were submitted to a special issue of *Progress in Oceanography*, and 8 papers have been accepted to date. The volume will be published in 2005.

Progress report of the SERIES data synthesis and publication (Agenda Item 6)

In the summer of 2002, a joint Canada/Japan iron enrichment experiment (**S**ubarctic **E**cosystem **R**esponse to **I**ron **E**nrichment **S**tudy – SERIES) was carried out in the eastern subarctic Pacific. A synthesis paper on the experiment was published in *Nature* (Boyd *et al*. "Evolution, decline and fate of an iron-induced subarctic phytoplankton bloom", Vol. 428: 549–553, 2004). In early April of 2004, a 3-day writing workshop was held at the Institute of Ocean Sciences, Sidney, Canada, to encourage data discussion, synthesis, paper outlines and writing. The workshop was successful and worthwhile. To date, 8 papers have been submitted to a special issue of *Deep-Sea Research II* (Guest Editors: P.J. Harrison, M. Levasseur, P. Boyd, R. Rivkin, A. Tsuda, and W. Miller), and about 8–10 papers are

coming in October 2004. There are still 17 proposed papers to be submitted, so a second volume would be proposed for 2005.

Preliminary report of SEEDS-II in 2004 (Agenda Item 7)

The second *in situ* iron enrichment experiment (joint Japan/US effort) was conducted in the western subarctic gyre of the North Pacific (48°10'N, 166°E) from July 20 to August 20, 2004. The experiment consisted of two iron additions: (1) 1600 kg of $FeSO_4 \times 7H_2O$ with an inert tracer gas SF_6, over an 8×8 km patch with a mixed layer depth of 30 m on Day 0 and (2) 790 kg of $FeSO_4 \times 7H_2O$ on Day 6. After the iron release, significant increase in dissolved iron concentration (1.4 nM on Day 1 and 0.6 nM on Day 7) was observed. Chlorophyll *a* concentration in the surface mixed layer increased from day 4 and reached >2.5 mg m^{-3} on Day 8, but these responses were relatively small compared with large increases observed during previous SEEDS-I experiment (about 20 mg m^{-3}). Size structure of phytoplankton was also different from SEEDS-I, and <10 µm size fraction accounted for 70–80% of the Chlorophyll *a* biomass throughout the observation period. Diatoms did not dominate in the phytoplankton community and decreases in nitrate and silicate concentrations in the surface water were minimum. The observed differences between SEEDS-I and SEEDS-II suggest a need to develop new hypotheses to explain how plankton assemblage responds to iron supply in high-nutrient, low-chlorophyll waters in the subarctic North Pacific.

Expansion of the terms of references (Agenda Item 8)

Due to the unexpected outcomes of the three meso-scale iron enrichment experiments, the Advisory Panel felt that it is important to expand the existing terms of reference (*IFEP-AP Endnote 3*) to include the following item:

- To synthesize, compare and contrast the results of SEEDS-I & II and SERIES, and to develop new experimental strategies and hypotheses to explain the different biogeochemical responses to iron enrichment.

IFEP-AP Workplan for 2005 (Agenda Item 9)

The following plans were outlined:

PICES XIV

- Conduct a ½-day IFEP/MODEL workshop on "Modeling and iron biogeochemistry: How far apart are we?" to enhance communication between experimentalists and modelers, and to establish a framework for organizing a 2–3 day workshop that will address problems on structuring iron biochemical models (*IFEP Endnote 4*).

Inter-sessional meeting

- Co-sponsor jointly with the Ocean Research Institute (University of Tokyo), a 2-day international symposium on SEEDS-II experiment, to be held in October 2005, in Tokyo, Japan. The goals of this symposium are: (1) to synthesize results from the second *in situ* iron enrichment experiments in the western subarctic North Pacific (SEEDS-II); and (2) to discuss differences in magnitude, biology and export between SEEDS-I and SEEDS-II.

Publications

- Selected papers from the SERIES iron enrichment experiment to be published as a special *Deep-Sea Research II* issue in 2005.
- A 5-year synthesis report of the Advisory Panel to be prepared for publication in the PICES Scientific Report Series. It will include circumstances of IFEP, summary of SEEDS-I & II and SERIES, terms of reference (initial and new), and future plans to understand why the three iron enrichment experiments in the subarctic North Pacific are different in magnitude, biology and export.

The Advisory Panel recognized the importance and need for holding a special symposium or session on three successful meso-scale iron enrichment experiments in the subarctic North Pacific (SEEDS-I & II and SERIES). It is, however, not the right time yet to convene such a symposium/session because the sample analyses and data synthesis of SEEDS-II are still underway. The Advisory Panel decided to postpone the special symposium/session to 2006 or later.

Requests for travel (Agenda Item 10)

The IFEP-AP requests support for the following travel:

- 2 scientists to attend the joint IFEP/MODEL workshop "Modeling and iron biogeochemistry: How far apart are we?" at PICES XIV;
- 1 invited speaker for the symposium on SEEDS-II to be held in Tokyo, Japan, in October 2005.

IFEP-AP Endnote 1

Participation List

Members

William P. Cochlan (U.S.A.)
Hiroaki Saito (Japan)
Shigenobu Takeda (Japan, Co-Chairman)
Mark L. Wells (U.S.A.)

Observers

Fei Chai (U.S.A.)
James Christian (Canada)
William R. Crawford (Canada)
Debby Ianson (Canada)
Jun Nishioka (Japan)
Angelica Peña (Canada)
Yasuhiro Yamanaka (Japan)

IFEP-AP Endnote 2

IFEP-AP Meeting Agenda

1. Round-table introduction of attendees
2. Adoption of agenda
3. Review of the IFEP activities in 2004
4. Report of the 2004 PICES-IFEP Workshop
5. Progress report of the SEEDS-I data synthesis and publication
6. Progress report of the SERIES data synthesis and publication
7. Preliminary report of SEEDS-II in 2004
8. Future perspective
9. Plans for 2005
10. Requests for travel supports
11. Other new business

IFEP-AP Endnote 3

Terms of Reference for Advisory Panel on
Iron fertilization experiment in the subarctic Pacific Ocean

1. To examine the reasoning for a subarctic iron enhancement experiment;
2. To examine the scale, disciplines, and resources (personnel and ships) required ensuring success of the experiment;
3. To design the experiment and its timing, particularly, the suite of chemical measurements and forms of iron, the biological parameters, the tracking of the spread of iron-induced bloom using SF_6 tracer;
4. To synthesize, compare and contrast the results of conducted experiments (SEEDS-I & II and SERIES), and to develop new experimental strategies and hypotheses to explain the different biogeochemical responses to iron enrichment (New).

IFEP-AP Endnote 4

Proposal for a ½-day IFEP/MODEL workshop at PICES XIV on "Modeling and iron biogeochemistry: How far apart are we?"

Synthesis of data from three successful meso-scale iron enrichment experiments in the subarctic North Pacific (SEEDS-I, SEEDS-II and SERIES) is underway. This workshop will enhance communication between experimentalists and modelers. For the most part, iron is not explicitly represented in current ecological models. The goal of this workshop will be to examine the structure of iron biochemical models with respect to what is known about iron biogeochemistry. The purpose will be to establish a framework for organizing a 2–3 day workshop that will address this problem in detail and compare ecological models that describe how plankton ecosystem respond to meso-scale iron enrichment in the high-nutrient, low-chlorophyll waters of the subarctic Pacific.
Recommended convenors: Fei Chai (U.S.A) and Shigenobu Takeda (Japan). MODEL has been approached to co-sponsor the workshop.

Travel support is requested for two scientists to attend the workshop, one expert on iron biogeochemistry and another on ecological modeling.

APPENDIX 5

PICES Press Articles

Subarctic Pacific Iron Experiment for Ecosystem Dynamics Study (SEEDS) in the western North Pacific, summer 2001

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Participants of SEEDS cruise after the experiment, forming a Chinese character for "iron" by men on the FRV Kaiyo Maru, *August 2001.*

Iron limitation has been proposed as the reason for the existence of surface waters rich in macro-nutrients but low in phytoplankton biomass in the subarctic Pacific, the equatorial Pacific and the Southern Ocean. Recent *in situ* iron enrichment experiments confirmed this in the equatorial Pacific and the Southern Ocean. In the subarctic Pacific, with biology and water structure different from the other two regions, strong zonal gradients in atmospheric iron deposition existing between the eastern and western gyres may give rise to distinct phytoplankton communities that characterize these biogeochemical provinces. Here we present an overview of SEEDS (Subarctic Pacific Iron Experiment for Ecosystem Dynamics Study), the first *in situ* test of the iron limitation hypothesis on natural ecosystem and geochemical cycles in the subarctic Pacific, which was funded by the Ministry of Environment of Japan for 3 years. SEEDS 2001 was originally proposed by the Advisory Panel on An Iron Fertilization Experiment in the Subarctic Pacific Ocean (IFEP) at the PICES Eighth Annual Meeting in Vladivostok, Russia, but the funding and ship opportunity were fixed only in March 2001. Then, we started and rushed for preparations of the experiment.

FRV *Kaiyo Maru* of Fisheries Agency of Japan departed from Tokyo on June 28, with full loading of experimental equipment and materials (17 large trucks: new record of *Kaiyo Maru*!). Seventeen researchers from the Fisheries Research Agency, the Central Research Institute of Electric Power Industry, the National Institute for Environmental Studies, Hokkaido University, Nagoya University, University of Kyoto and University of Tokyo participated in the cruise. The first leg of the cruise was allotted for physical and biochemical survey of the target area, and performance tests of newly designed equipment such as the continuous measurement system of an inert tracer gas sulphur hexafluoride (SF_6), and the iron/SF_6 mixing and injection system.

During the second leg of the cruise, a meso-scale *in situ* iron enrichment experiment was conducted in the western subarctic gyre of the North Pacific (48.5ºN, 165ºE) from July 18 to August 1, 2001 (Fig. 1). The experiment consisted of a single addition of 350 kg iron as $FeSO_4$ (10,800 L of 0.5 M Fe) with 4100 L of SF_6 saturated seawater, over an 8×10 km patch with a mixed layer depth of 10 to 15 m. Using the GPS buoy-Lagrangian navigation system, the solution of iron and SF_6 mixed at a constant ratio was released under the ship's propellers within 24 hours. Initial concentration of dissolved iron in the iron-enriched patch was about 1.9 nM (mean value of day-1 underway transect; maximum recorded was 6.0 nM).

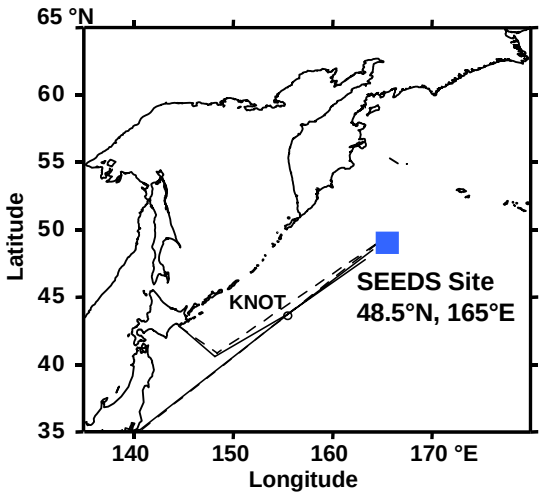

Fig.1 Location of SEEDS iron enrichment experiment.

The weather was foggy but calm throughout the observation period, which was lucky for the participants in the cruise but less than ideal for satellite observation of the iron patch. The iron-enriched patch moved westward during the experiment, but we could successfully trace the iron-enriched patch for a 2-week observation period by measuring SF_6 in surface waters. Along with continuous surface measurements of SF_6 and iron concentrations, a fast repetitive-rate (FRR) fluorometer, which measures community photosynthetic competency (Fv/Fm), and an underway pCO_2 system, also provided real-time mapping. The first indication of a phytoplankton response to iron enrichment was a significant increase in Fv/Fm measured by the FRR fluorometer on the night of day-3, and the scientists on board get excited. By day 10, we observed unambiguous and massive biogeochemical responses to the iron addition, which resulted in an increase in chlorophyll *a* concentrations to as high as 20 µg/l, and large drawdowns in pCO_2 dioxide and nutrients (Fig. 2).

The iron-enriched water became a rich-soup of phytoplankton, and a change in the water color was recognizable for everyone after day-9 (Fig. 3). In addition, iron supply led to floristic shifts that resulted in the dominance of chain-forming large centric diatoms, unlike the equatorial Pacific and the Southern Ocean where iron stimulated the growth of pennate diatoms. We finished our observation with trawl sampling of salmons and other nekton in and out of the patch on day-14. The water mass with high chlorophyll and low pCO_2 was still there, but we had to leave.

Our initial findings clearly demonstrate that iron availability fundamentally controls the magnitude of phytoplankton response in high nutrient areas of the western subarctic Pacific. Analysis of samples from this experiment will also help to clarify the role which iron plays in regulating the biogeochemical processes such as export production. Furthermore, we realize that we need longer and more intense observation of the iron-enriched patch to understand the ecosystem-scale response to iron input, and the fate of accumulated organic carbon after the end of diatom blooming, which might only be possible with international cooperation.

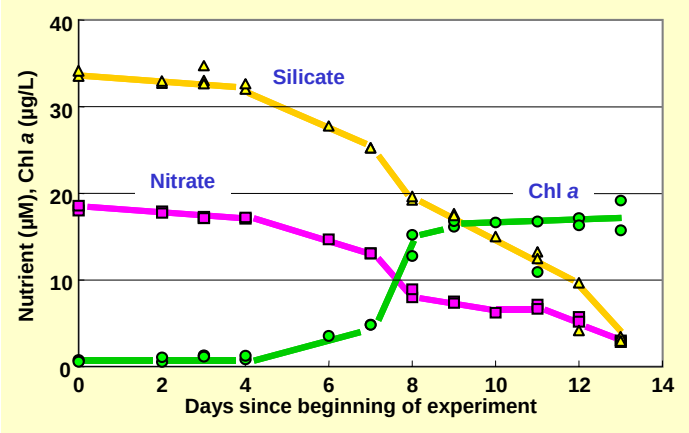

Fig.2 *Changes in chlorophyll* a, *nitrate and silicate concentrations measured in the iron-enriched patch during SEEDS 2001.*

Fig. 3 *Comparison of water color between the outside (top panel) and inside (bottom panel) of the iron-enriched patch on day-14. (Photo by H. Kiyosawa)*

Plans for the Canadian SOLAS Iron Enrichment Experiment

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There are large areas of the North Pacific Ocean where iron limits primary productivity. At Ocean Station Papa (OSP; 50°N and 145°W) (Fig. 1), several iron enrichment experiments in carboys on board ship have demonstrated that in May/June and August/September, when 2-4 nM Fe is added to surface water, chlorophyll increases several fold and mainly pennate diatoms dominate the phytoplankton assemblage (Boyd et al. 1996. In vitro iron enrichment experiments in the NE subarctic Pacific. Mar. Ecol. Prog. Ser. 136: 179-193). These pennate diatoms do not appear to be eaten by the ambient mesozooplankton and likely sink when they have used up the added iron (Harrison et al. 1999. Comparison of factors controlling phytoplankton productivity in the NE and NW subarctic Pacific gyres. Prog. Oceanogr. 43: 205-234). However, it is not possible to measure the broader ecosystem response and carbon flux in carboy experiments. As the next step in the study of the ecosystem response to an iron addition at OSP, we proposed a large-scale open ocean iron enrichment, similar to IRONEX I and II, SOIREE and, more recently, the successful Japanese SEEDS experiment (this issue). These plans were initiated by the Advisory Panel on An Iron Fertilization Experiment in the Subarctic Pacific Ocean (IFEP) at the PICES Eighth Annual Meeting in Vladivostok, Russia, in October 1999 (for details see PICES 1999 Annual Report, pp. 108-110). Plans were further developed at the special IFEP Planning Workshop on "Designing the iron fertilization experiment in the Subarctic Pacific" that was held in October 2000, in Tsukuba, Japan, in association with the PICES Ninth Annual Meeting (for details see PICES 2000 Annual Report, pp. 89-95).

This year we received funding from the Natural Sciences and Engineering Research Council of Canada (NSERC) and Panel for Energy Research and Development (PERD) of Natural Resources Canada (NRCan) to Fisheries and Oceans Canada. This funding is part of the Canadian SOLAS (Surface Ocean Lower Atmosphere) program and it will form a contribution to the International SOLAS project, a new core project under the International Geosphere Biosphere Program. The main objective of the International and Canadian SOLAS program is to address the key interactions among the marine biogeochemical system, the atmosphere, and climate. One of the highlights of the Canadian SOLAS program is that it will bring the atmospheric scientists and the oceanographers together for the first time in this coordinated project. At OSP, we will test how an addition of iron (as a simulation of natural Fe additions via dust or offshore eddies) will increase primary productivity, the production of trace gases such as dimethylsulphide (DMS) and organic halides and the drawdown of CO_2, all of which can influence climate. We have adopted the acronym SERIES (Subarctic Ecosystem Response to Iron Enrichment Study) for our iron enrichment experiment.

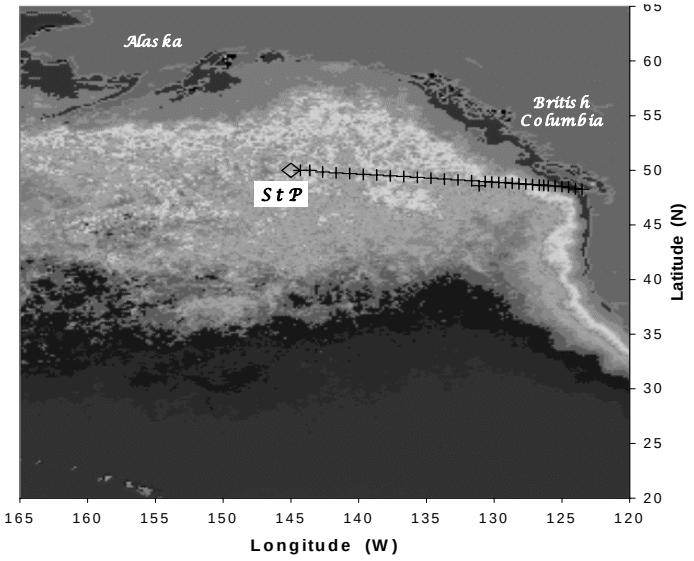

Fig. 1 CZCS annual chlorophyll distribution in the NE Pacific. Line P stations (+) and Ocean Station Papa, which are sampled three times annually to provide time-series measurements of ocean variability, are indicated.

In July 2002, we will collaborate with scientists from Japan and the United States to conduct an open ocean iron enrichment experiment at OSP. There will be two ships, Canadian CCS John P. Tully and Mexican R/V El Puma (Figs. 2 and 3), that will provide about 40 berths. We plan to enrich a 100-km^2 patch of the ocean and follow it for 2 to 3 weeks. Japanese scientists will visit OSP and extend the sampling time along with the US scientists (if they receive funding). This extension in following the patch should allow us to determine the fate of the bloom.

Fig. 2 The CGSS John P Tully, a 69 m research vessel operated by Fisheries and Oceans Canada to conduct oceanographic programs in the North Pacific.

We will measure a wide range of parameters to determine the response of the plankton community to the iron addition, the fate of carbon (drawdown of CO_2 and carbon export), production of trace gases (DMS, N_2O and organic halides), iron chemistry (including iron complexation and the longevity of the bloom), and exchange processes at the air/sea interface. The field data will ultimately be integrated into coupled ocean and atmosphere models.

Fig. 3 The 50 m long R/V El Puma, the Pacific Coast vessel operated by the National University of Mexico (UNAM) to conduct oceanographic programs in the Pacific

Our results will provide a very interesting comparison between the response of the NE (Canadian SOLAS) and NW (SEEDS Japan) subarctic Pacific gyres to iron enrichment. The NW gyre is less iron-limited since it is closer to an iron source, the dust from the Gobi Desert in China. The two gyres present a natural gradient of iron limitation and hence a different ecosystem response is expected to the iron enrichment.

PICES-IFEP Workshop on "In-situ *iron enrichment experiments in the eastern and western subarctic Pacific*"

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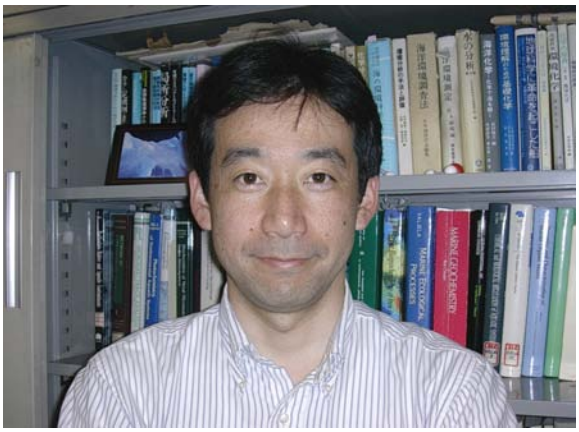

Dr. Shigenobu Takeda is an associate professor of Aquatic Biology and Environmental Science Laboratory, Graduate School of Agricultural and Life Sciences, University of Tokyo. His research interests include trace metals-phytoplankton interaction, biogeochemical cycles of iron, behaviour of silicon and other trace elements in the ocean, and eutrophication processes in coastal systems. Within PICES, Shigenobu is the Co-Chairman of the Advisory Panel on Iron Fertilization Experiment.

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Dr. C.S. Wong is a senior research scientist and team leader of the Climate Chemistry Laboratory at the Institute of Ocean Sciences. His research focuses on the oceanic carbon cycle, halocarbon and isotopic tracers, iron fertilization and mitigation CO_2 in the oceans. He co-chairs the PICES Advisory Panel on Iron Fertilization Experiment, *and is also a member of the PICES Physical Oceanography and Climate Committee and WG 17 on* Biogeochemical data integration and synthesis.

Iron deficiency has been proposed as the reason for the existence of surface waters rich in macro-nutrients but low in phytoplankton biomass in the subarctic Pacific, the equatorial Pacific and the Southern Ocean. In summer of 2001, an iron enrichment experiment (**S**ubarctic Pacific Iron **E**xperiment for **E**cosystem **D**ynamics **S**tudy – SEEDS-I) was performed in the western subarctic Pacific; and in summer of 2002, another iron enrichment experiment (**S**ubarctic **E**cosystem **R**esponse to **I**ron **E**nrichment **S**tudy - SERIES) was carried out in the eastern subarctic Pacific. These international collaborative projects between Canada and Japan were conceived at the first planning workshop of the PICES Advisory Panel on *Iron Fertilization Experiment* (IFEP), held in Tsukuba, Japan, in 2000, in conjunction with PICES IX.

In order to review the results and outstanding questions from these experiments and to discuss plans for the second longer-term experiment in the western subarctic Pacific (SEEDS-II), the PICES-IFEP Workshop on "*In situ* iron enrichment experiments in the eastern and western subarctic Pacific" was held February 11-13, 2004, at the Chateau Victoria Hotel, Victoria, British Columbia, Canada. 26 scientists from Canada, Japan, and the United States of America attended the workshop (Fig. 1).

The objectives of the workshop were to:

- Synthesize results from the two *in situ* iron enrichment experiments performed in the eastern and western subarctic Pacific (SEEDS-I and SERIES);
- Discuss responses to iron additions in lower and higher trophic levels, carbon cycles, trace-gas production and ocean-atmosphere flux, and models;
- Determine similarities and differences in biogeo-chemical and ecosystem responses to iron addition between the eastern and western subarctic Pacific;
- Identify specific scientific questions for the new longer-term experiment in the western subarctic Pacific (SEEDS-II).

The workshop started with 4 synthesis talks on SEEDS-I, SERIES and SOFeX, followed by 14 shorter presentations

Fig. 1 Workshop participants at the entrance of the Chateau Victoria Hotel

on the physical behavior of the Fe-enriched patch, biological/physiological responses, food-web dynamics, chemistry of iron, carbon cycle, and model prediction.

What have we learned from the enrichment experiments?

Both SEEDS-I and SERIES have demonstrated increased productivity and biomass of phytoplankton as a response to the iron enrichment. Bloom evolution and decline was captured in detail during SERIES. However, there are differences in the physical and chemical environments, the plankton ecosystem and dominant species, and zonal iron gradient between the Western Subarctic Gyre (WSG) and the Alaskan Gyre (AG). From SEEDS-I and SERIES, we can point out the following similarities and differences in biogeochemical and ecosystem responses to iron addition:

Similarities

- Diatom bloom occurred; floristic shift to large cells;
- Vertically-integrated Chl-*a* and primary production increased;
- Heterotrophic dinoflagellates grazed on diatoms after the development of the bloom, and led to significant loss of diatoms in the mixed layer;
- Copepods were not the primary grazers; SERIES was not well matched with the spring period of maximum diatom grazing (*Neocalanus plumchrus*);
- DOC (dissolved organic carbon) increased during the growth phase of bloom, was constant through the stationary phase, and decreased during the bloom decline; DOC production was about 10% of primary production;
- Increased dissolved-Fe was mainly in colloidal fraction;
- Dissolved-Fe concentration decreased rapidly by colloidal aggregation and biological uptake (less), and loss rate gradually decreased;
- Particulate-Fe concentrations remained high; bioavailability of remaining iron (mainly particulate) was low;
- Majority of macro-nutrients were consumed;
- Increase in Si/NO_3 drawdown ratio was observed after occurrence of physiological stress such as iron and light limitations.

Differences

- A larger and faster response (in terms of biomass) was observed in WSG;
- Initial diatom populations largely neritic for WSG and pelagic for AG; neritic species responded quickly to the iron enrichment and built up a large biomass, suggesting that the presence of coastal species as resting spores or cells is important in determining the magnitude of bloom evolution;
- The bloom was characterized by two ecological phases in SERIES. Phase I consisted of nano-phytoplankton (prymnesiophytes) and occurred before day 10 of the experiment, and phase II was mainly diatoms and began after day 10;
- Sediment traps collected large $CaCO_3$ fluxes after phase I, and high biogenic-Si and POC fluxes after phase II during SERIES, but not in SEEDS-I. SEEDS-I occupation may have been too short to observe export event;

- >50% of the mixed-layer POC (particulate organic carbon) deficit attributed to bacterial re-mineralization and meso-zooplankton grazing in AG; NH_4 in surface waters increased throughout the bloom;
- Characteristics of organic ligands changed rapidly upon Fe enrichment in WSG; ligands concentration tracked dissolved-Fe concentration in AG, rapidly disappearing together with dissolved-Fe concentration;
- The iron enrichment created a bloom of DMSP-rich nano-phytoplankton (*E. huxleyi*) which crashed after day 11 in SERIES, but no significant increase in DMS/DMSP was observed in WSG;
- The Fe-induced increase in DMSP had no clear effect on DMS concentrations in AG;
- The iron-induced deficit in DMS concentrations during the peak of the diatom bloom resulted from a decrease in biological DMS net production in AG.

Kenneth Coale was invited to give a synthesis talk on Southern Ocean Iron Experiment (SOFeX), which was performed in 2002, to investigate the effects of iron enrichment in regions with high and low concentrations of silicic acid. He identified the following questions to be resolved in future experiments.

- What are Fe:C:Si:N:P uptake and re-generation stoichiometries? How are these stoichiometries related to phytoplankton community structure?
- What is the steady-state condition? Is this a relevant question?
- What is the periodicity and magnitude of natural iron enrichment, both seasonally and inter-annually, and on glacial-interglacial time scales?
- What is the effect of iron enrichment on the geochemistry (low O_2 and de-nitrification) and ecology (nitrification) below and within the Fe patch?
- Do ecosystems respond in a natural manner to artificial Fe enrichments? What are the similarities and differences between natural and artificial Fe supply?

What are outstanding questions?

SEEDS-II is the second meso-scale iron enrichment experiment in WSG designed to investigate the longer-term effects of iron enrichment on plankton ecosystem, carbon export and trace gas production. SEEDS-II will involve about 50 researchers from universities and government institutions in Japan, the United States and Canada. The iron-enriched patch will be monitored by two ships, the R/V *Hakuho Maru* (Japan) and the R/V *Kilo Moana* (U.S.A.), for 34 days from July 21 to August 23, 2004. Through the integration and synthesis of the findings from SEEDS-I, SERIES and SOFeX, the workshop participants identified the following key themes and key scientific questions for the SEEDS-II experiment.

Fate of carbon

- What portions of organic carbon fixed by coastal centric diatoms in WSG will be exported from the surface mixed layer, and what portions will be regenerated?
- To what extent would heterotrophic dinoflagellates (*Gyrodinium*) respire Fe-induced carbon fixation?
- What is turnover time of produced DOC?
- What are community respiration rates?
- Is C:N:P:Si regeneration ratios in surface and subsurface layers crucial to our understanding of Fe-induced ecological response and nutrient dynamics?
- Is biological patchiness in species and export within the patch significant?
- How does physical dilution from outside affect the patch chemistry and biology? What is the effect of dilution on budget calculations?

Ecosystem responses

- Why did SEEDS-I and SERIES have opposite trends in dominant diatom composition?
- What is the role of cell lysis on changes in available nutrients, sources of DMSP, bacterial community structure and iron chemistry?
- What roles will sinking and grazing play in the decline of the bloom?
- What is the long-term effect of Fe availability on the ecosystem? How is the response to further iron addition affected?
- The ecological response to iron enrichment is largely determined by the seed population. What will the species variability and ecosystem differences be between iron-induced blooms in the same location?
- How predictable will the species response be to iron addition?
- Why does Fe addition to bottles result in N-limitation, but the large-scale Fe additions show Si-depletion?

Seasonal timing

- If natural events occur, should we try to emulate those that occur at other times of the year?
- What is the importance of the presence of endemic zooplankton at the time of iron enrichment?

Fe biogeochemistry

- What controls iron retention and loss after iron release?
- What is the main source of ligands production? How does it respond to iron enrichment?
- What is the role of iron ligands in Fe bioavailability and recycling?
- What is the role of Fe(II) in the phytoplankton bloom?
- What is the uptake of iron by different biota?
- What is the difference between single and multiple iron additions, and their effect on availability of iron?
- Comparison with natural iron supply: labile particulate iron was significantly higher in the surface mixed layer in WSG, but dissolved iron was at the same level as in the eastern region.
- Is bioavailability of iron (not total iron input) most important for ecosystem response?

Trace-gas production

- What is the fate of DMSP? Is it consumed by bacteria? Does it sink?
- What are the roles of physiological stress, Fe availability, light and macronutrients on DMSP cycling?
- What is the extent of emission to atmosphere?

Recommendations for SEEDS-II

- It was recommended to lengthen the experiment if possible; the decline will depend on patch physical dynamics, bloom dynamics, etc.
- Additional suite of measurements is required to study bloom evolution, including FRRF, Flavodoxin, sinking rates, TEPS, and supplement these with ^{15}N and ^{32}Si uptake rates;
- Additional methods are required to determine the role of the microbial community and zooplankton in the fate of POC and O_2 profiles of the upper ocean, community respiration, labelled particle decomposition experiments;
- Additional experiments are required for measuring export flux, such as trap calibration with thorium, large-volume pump thorium samples, more fluorometers for the upper trap moorings;
- Estimates of silica dissolution, bacterial production and respiration, and bacterial Fe-stress should occur;
- Measurements of micro- and meso-zooplankton grazing, and the prey (including particles are desirable.

Thanks to the excellent presentations and spirited discussion from all participants, the workshop was very successful. The results of the workshop will be published as a PICES Scientific Report in 2004.

Canadian SOLAS/PICES-IFEP session on *"Response of the upper ocean to meso-scale iron enrichment"*

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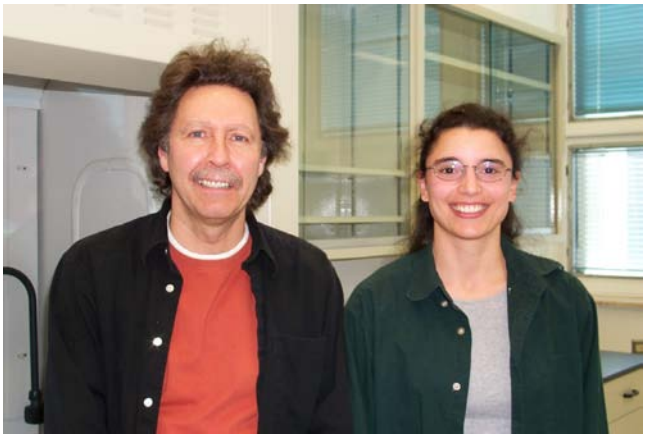

Dr. Maurice Levasseur is a professor in the Department of Biology at Université Lava, where he leads the Canadian Chair on Climate Variability and Plankton Ecosystems. He is also the Chairman of the Canadian SOLAS Network (csolas.dal.ca). His research focuses on the marine production of the climatically-active gases and the eco-physiology of harmful algal blooms. Within PICES, Maurice has been involved in activities of the Advisory Panel on Iron Fertilization Experiment *and the Working Group on* Ecology of the Harmful Algal Blooms in the North Pacific.

Anissa Merzouk graduated with a B.Sc. in Marine Biology from the Université du Québec à Rimouski. She is currently completing a Ph.D. in Oceanography at Université Laval under the supervision of Prof. Levasseur, working on understanding the controls of the biological production and consumption of DMSP and DMS in surface waters. Within the C-SOLAS program, she participated in the SERIES iron enrichment experiment in the NE Pacific to determine the influence of iron on the distribution and biological cycling of DMSP and DMS.

Background

The productivity of large portions of the global ocean is thought to be limited by the availability of iron, a micronutrient essential to phytoplankton growth. So far, eight meso-scale iron fertilization experiments have been conducted in order to test this hypothesis, and to provide insights on the potential effect of iron addition on algal blooms development and the biogeochemical cycle of major elements, with a special focus on climatically-active gases, such as CO_2 and dimethylsulfide (DMS). Two of these recent experiments conducted in the North Pacific were developed under the umbrella of PICES, through its Advisory Panel on *Iron Fertilisation Experiment*, co-chaired by Drs. Shigenobu Takeda and C.S. Wong. These experiments took place in 2001 in the Northwest Pacific (SEEDS), and in 2002 in the Northeast Pacific (SERIES). Both experiments were successful and generated important new findings (Tsuda *et al.* 2003. A mesoscale iron enrichment in the western subarctic Pacific induces large centric diatom bloom. Science, 300: 958-961; Boyd *et al.* 2004. Evolution, decline and fate of an iron-induced subarctic phytoplankton bloom. Nature, 428: 549-553).

Meso-scale experiments are costly, involve many scientists and generate huge volumes of data. It is our responsibility to maximize the diffusion of this information and to ensure a skilful utilization of these unique data sets. A group of research scientists involved in the planning and realization of these experiments thought that the timing was good to synthesize and compare the responses obtained so far during these experiments. To accomplish this task a joint C-SOLAS/PICES-IFEP session on "*Response of the upper ocean to meso-scale iron enrichment*" was convened on February 17-18, during the ASLO/TOS 2004 Ocean Research Conference held in Honolulu, Hawaii (session organizers: Maurice Levasseur, Atsushi Tsuda, William Miller, William Cochlan and Richard Rivkin).

The call for papers was very well received, resulting in a session composed of 23 oral presentations and 17 posters. As expected, the session was a showcase for the most recent experiment: SERIES. But there was also significant contribution from SEEDS and SOFeX, and some presentations proposed thoughtful inter-comparisons between the various meso-scale experiments. This special session allowed to recognize the similarities and differences in the responses obtained from these experiments.

Overview of presentations

The session started with a tutorial by Kenneth Coale who presented a synthesis of the knowledge gained from the seven mesoscale iron enrichments experiments conducted so far, pointing at similarities but also emphasizing that each experiment was unique in terms of location, season and initial conditions, and thus generated different responses to iron enrichment. The take home message was that although we know much more than 10 years ago, much remains to be understood in order to properly evaluate the global impact of iron on ocean biogeochemical cycles and climate.

The tutorial was followed by 4 talks on SOFeX, highlighting new outcomes from this expedition in the Southern Ocean. William Cochlan showed that there was a clear change in the relative utilization of new and re-generated nitrogen following the iron fertilization, with nitrate uptake increasing by 15-fold and 25-fold north and south of the Antarctic Polar Front Zone (APFZ), respectively. Stephen Baines reported on iron-induced changes in the elemental stoichiometries of individual diatoms and flagellates using a synchrotron x-ray fluorescence microprobe. His results indicate biochemical changes in the resident plankton, suggesting differences in the biogeochemistry of Fe-replete and Fe-deplete regions of the ocean. Mark Brzezinski showed that iron fertilization caused a shift from non-Redfield to Redfield nutrient uptake ratios in the Southern Ocean, shifts that will have strong implications for elemental cycling and climate during periods of enhanced Fe supply. Finally, Michael Hiscock demonstrated that iron addition resulted in an increase in the maximum quantum yield of photosynthesis, but that the intensity of the response varied within size fractions between the nitrate-rich and silicate-rich in the waters north and south of the APFZ. These presentations, along with the companion posters, highlighted important regional variability in the responses of the plankton community to iron fertilization in the Southern Ocean.

The next 2 talks, accompanied by 4 posters, reported more specifically on the SEEDS expedition conducted in the NW Pacific in 2001. Atsushi Tsuda gave an overview of SEEDS where the iron fertilization induced a large centric diatom bloom resulting in a marked consumption of macronutrients, a huge increase (factor ~ 20) in chlorophyll *a* concentrations and a marked drawdown in pCO_2. By day 13 of the experiment, the export of fixed carbon represented only 13% of the primary production in the iron-enriched patch, with most of POC (particular organic carbon) remaining in the surface mixed layer. The fate of the bloom remains unknown. Isao Kudo presented interesting results on the effect of water temperature on the response of the phytoplankton community to iron addition obtained in shipboard experiments performed during SEEDS and SERIES. The phytoplankton growth rate in the fraction of >10 μm was higher in the NW Pacific than in the NE Pacific for similar iron addition and temperature (12°C). Since surface temperature increased from 5 to 9°C in the weeks before the SEEDS experiment, he hypothesized that the growth rate dependence on temperature could explain the exceptionally large increase in chlorophyll *a* and primary production measured during SEEDS. Jun Nishioka presented a poster on the distribution of size-fractionated iron and showed that iron supply is higher in the NW Pacific than in the NE Pacific due to more frequent atmospheric inputs. During SEEDS, the added dissolved iron was rapidly transformed to labile particulate iron, reducing its bio-availability to phytoplankton, a process that probably also occurs for dissolved iron originating from atmospheric inputs. In his poster, Takeshi Yoshimura demonstrated that in the NW Pacific, 10 to 20% of the net organic carbon production was converted to DOC (dissolved organic carbon) during the growth and stationary phases of the bloom. In the NE Pacific, the net DOC production was higher during the decline phase of the bloom, suggesting the domination of decomposition processes. Hiroaki Saito's poster suggested that phytoplankton growth exceeded micro-zooplankton grazing at the beginning of the SEEDS experiment, but micro-zooplankton grazing rates and phytoplankton grazing mortality increased rapidly at the end of the experiment. These results highlighted the balance between phytoplankton growth and loss due to grazing, and how this equilibrium may be affected by iron. Naoki Yoshie presented a poster on the modeling of the SEEDS diatom bloom. The model successfully reproduced the vertical distributions of macronutrients and chlorophyll during the evolution of the bloom. The model predicts that the effect of iron on the ecosystem would last for 40 days, and that the export flux during the 13-day observation period represents 20 to 30% of the export predicted for 40 days.

The following 15 oral presentations (with 5 posters) reported on SERIES, the most recent meso-scale iron enrichment experiment at that time. This block of talks began with an overview of SERIES by Phillip Boyd, who presented the evolution, decline and fate of the SERIES bloom. His talk was completed by the presentation of David Timothy on the nutrient dynamics, uptake and export of carbon and biogenic silica. Their results showed that the termination of the diatom bloom was due to iron limitation followed by silicic acid limitation. More than half of the carbon fixed by the bloom was grazed or re-mineralized by bacteria and only a small portion of the bloom's particulate carbon (18%) and biogenic silica (34%) was exported from surface waters (>50 m). Jean-Eric Tremblay presented data on phytoplankton growth and nutrient uptake ratios during the evolution of the bloom. The nano-phytoplankton bloom was initiated by increased growth rates immediately after iron addition, and was halted by grazing losses. A presentation by Nelson Sherry and a poster by Paul Harrison described the shift in phytoplankton community composition from small nano-phytoplankton (flagellates) to large pennate diatoms. Chlorophyll *a* and primary production increased rapidly during the diatom bloom in parallel with a drawdown of macronutrients. Adrian Marchetti presented field and lab data on elemental composition ratios in a diatom, showing that iron-limitation resulted in an increase of the Si/N ratio due to a decrease in N-uptake. He concluded that diatoms were iron-stressed before the full depletion of silicic acid during SERIES.

Richard Rivkin presented an insightful synthesis of the influence of iron on bacterial stocks and processes during different meso-scale iron enrichments. Iron increased bacterial abundance and production during all fertilization experiments. The bacterial response during SERIES was markedly larger than in the Equatorial Pacific (IronEx II) and Southern Ocean (SOIREE), resulting in increased retention of carbon in the surface layer and reduced export to the deep ocean. Carol Adly and Michelle Hale presented posters on the bacterial response to iron enrichment. The first author reported a small but rapid increase in bacterial abundance and production immediately (few hours) after

iron enrichment, suggesting that bacteria were initially iron-limited. Hale's results showed that the bacteria were generally DOM-limited during the first days of the experiment. Bacterial production and growth rates peaked 6 days prior to the increase in biomass, suggesting that bacteria were under strong grazing pressure during the first 13 days of the bloom.

Sonia Michaud and Michel Scarratt presented results on the influence of iron on the dimethylsulfoniopropionate (DMSP) and dimethylsulfide (DMS) distribution during SERIES, and Anissa Merzouk presented data on DMSP and DMS biological cycling. The bacterial utilization of DMSP shifted from high DMS production in the sulfur-rich nano-phytoplankton bloom to low DMS production during the sulfur-poor diatom bloom, resulting in an overall DMS deficit in the iron-enriched patch. It is the first time that a negative effect of iron fertilization on DMS is observed. William Miller and Rene-Christian Bouillon showed that iron fertilization decreased the DMS photo-oxidation rate coefficient. They proposed that nitrate-photolysis played a significant role in DMS photo-degradation. Yvonnick. Le Clainche used an inverse modeling approach to show that the regional increase in DMS concentrations during SERIES resulted from a combination of low ventilation and high DMS biological net production.

Robert Moore presented data on the production and fluxes of isoprene and methyl-iodide, two atmospherically-reactive gases. The net production of isoprene and its flux to the atmosphere increased during the course of the experiment, whereas methyl-iodide concentrations were lower in-patch than out-patch. These gases were of biogenic origin but their production mechanisms are poorly understood.

Kenneth Denman presented the modeling of the plankton community structure during the iron enrichment. The model reproduced well the development of the bloom but not the export of carbon fixed by the diatom bloom, suggesting that processes such as aggregation may have played a role in increasing the export flux at the end of the bloom.

Less usual for an ASLO meeting, the last two talks reported on the influence of iron fertilization on the atmospheric distribution of DMS, methane sulfonic acid (MSA) and aerosols. Moire Wadleigh presented the sea-to-air DMS fluxes and atmospheric DMS concentrations, while Lisa Phinney reported on aerosol processing over the region of the SERIES experiment. DMS fluxes were correlated with seawater DMS concentrations and wind speeds. Atmospheric DMS, MSA and sulfate concentrations were high in the study area compared to mean worldwide values. DMS and its degradation products were particularly elevated during a regional episode of high seawater DMS concentrations around days 6-9.

Conclusions

Papers presented during the session revealed important similarities and differences in the responses to iron fertilization observed in the different high nutrient low chlorophyll (HNLC) oceanic regions. One noteworthy similarity is that the growth of phytoplankton from all size classes seemed to be stimulated by iron addition, with small flagellated cells blooming first, followed by the diatoms.

Although a decrease in pCO_2 is generally measured in those experiments, results from SERIES indicate a low carbon sequestration efficiency. Whether such low efficiency can be extrapolated to the other HNLC regions is uncertain since bloom termination was generally not monitored during previous experiments. Carbon sequestration may vary depending on the structure of the phytoplankton assemblage, the limiting nutrient (Fe, nitrate, silicate), grazing, respiration, *etc*. Since these conditions vary from one site to another, the efficiency of carbon sequestration is expected to change as well. There is thus a need to determine the fate of the bloom in the major HNLC regions.

In addition to altering the carbon cycle, iron fertilization may also affect the production of other climatically-active biogenic gases such as DMS. During SERIES, the iron-induced diatom bloom coincided with a decrease in DMS concentrations. This was a clear departure from previous experiments where iron addition resulted in an increase in DMS. Again, these conflicting results call for further experiments. In order to properly evaluate the global impact of iron on sea-to-air exchange of climatically-active gases, we need a minimum, but statistically sound, understanding of the sensitivity of the different HNLC regions to iron. This can only be achieved through repeated, well planned, experiments. Given that up to 40% of the ocean surface is limited by iron, these experiments are essential steps in our quest to understand past, present, and future climate.

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