

Dear The Editor and Anonymous Reviewers,

First of all, we greatly appreciate the time and effort spent in reviewing of our manuscript. Unfortunately, we recently heard that the Korean Iron Fertilization Experiment in the Southern Ocean (KIFES) project, which was the inspiration for this review, has lost its funding. However, we here at Korea Polar Research Institute, as well as our domestic and international collaborators, fully intend to seek other sources of funding to revitalize the KIFES project. We apologize in advance that our responses to reviewer questions on KIFES are necessarily vague due to the current state of uncertainty surrounding the future of the project (Reviewer 1- Comments 8, 9, 10, 11 and Reviewer 2- Comments 13-2, 24). Nevertheless, we believe that this manuscript is still worthy of publication as a detailed review of the history of ocean iron fertilization experiment designs and results. We have changed the title as follows: **“Ocean Iron Fertilization Experiment: Past-Present-Future looking to a future Korean Iron Fertilization Experiment in the Southern Ocean (KIFES) Project”** and still provide design guidelines for KIFES even though it is not presently funded.

- Response to Reviewer Comments -

5 Reviewer #1

-General Comments:

10 **1** *Downward carbon fluxes can be quantified using diverse metrics. The really important one from the point of view of geoengineering would be the amount of carbon sequestered below the depth of deepest winter mixing in the study region, which most previous OIF did not measure. The article frequently uses terms such as “efficiency of OIF at reducing atmospheric CO₂”, but the authors never define clearly what they mean by this. The efficiency of the biological carbon pump can be quantified using several approaches, but from a geoengineering point of view the efficiency is less important than the absolute amount. The article would be more helpful if the authors defined clearly which metrics really matter. Moreover, it would be useful if the authors more explicitly assessed which of the experiments conducted to date were actually capable of detecting an enhancement of export if it had occurred (based on duration of the experiment relative to the phases of the bloom and the type of measurements that were taken), which of these did find a response in particle flux (e.g. EIFEX, SERIES), and how to what depth the carbon flux was followed.*

→ Thank you for pointing this out. To reflect the Reviewer’s suggestion, we added the following to define the “effectiveness of OIF” in the Introduction:

20 - 1 Introduction (from line 40, page 2 to line 2, page 3):

“To evaluate whether OIF has potential as a geoengineering strategy for carbon sequestration, not only the amount of carbon fixed by phytoplankton at the ocean surface but also the amount of carbon sequestered to the deep ocean must be considered in determining the effectiveness of OIF (Buesseler and Boyd, 2003).”

25 → Based on the Reviewer’s comment, we have created a new “Table 5” (Please refer lines 1–5, page 36) that includes where available: absolute magnitude of export carbon flux; measurement depth; and the methods applied to detect an enhancement of export. Using “Table 5”, we also have created new Section “2.5 Assessment of export carbon flux” to more explicitly assess the enhancement of carbon flux in the manuscript as follows:

- 2.5 Assessment of export carbon flux (from line 21, page 9 to line 30, page 10):

30 “Early OIF experiments showed that iron addition stimulates the first step of the biological pump, promotion of phytoplankton growth. To determine whether the second step of the biological pump, export of carbon to the deep sea (i.e., increased export production), is enhanced after iron addition, the export flux of particulate organic carbon

(POC) has been estimated using, either together and/or individually, chemical tracers such as natural radiotracer thorium-234 (^{234}Th ; half-life = 24.1 days) and the stable carbon isotope of particulate organic matter ($^{13}\text{C}_{\text{org}}$), free-drifting sediment traps, beam-transmissometers, and underwater video profilers (UVP) (Table 5) (Bidigare et al., 1999; Nodder et al., 2001; Boyd et al., 2004; Buesseler et al., 2004; Coale et al., 2004; Aono et al., 2005; Tsuda et al., 2007; Smetacek et al., 2012; Martin et al., 2013).

The ^{234}Th isotope has a strong affinity for suspended particles, and the extent of ^{234}Th removal in the water column is indicative of the export production below the euphotic zone associated with surface primary productivity (Buesseler, 1998). In IronEx-2, which was the first OIF experiment in which POC flux was estimated, surface values were calculated from the so-called ^{234}Th activity balance method (Bidigare et al., 1999). The ^{234}Th deficiency of the surface ocean (25 m) during IronEx-2 was evident in the iron-fertilized patch, indicating iron-stimulated export production (Table 5). However, there were no ^{234}Th observations conducted in the unfertilized patch for comparison and nor were there observations to estimate downward POC export to the deep ocean (Bidigare et al., 1999).

SOIREE was first study to quantify downward export processes to the deep Southern Ocean using a comprehensive suite of methods such as ^{234}Th and $^{13}\text{C}_{\text{org}}$ estimates derived from high volume pump sampling, free-drifting sediment trap deployments, and beam transmissometer (Nodder and Waite, 2001). However, no measurable change in carbon export was observed in response to iron-stimulated primary production during the 13-day occupation of the SOIREE (Fig. 8b and Table 5) (Charette and Buesseler, 2000; Nodder and Waite, 2001; Trull and Armand, 2001; Waite and Nodder, 2001). For EisenEx, ^{234}Th observations showed no differences between in-patch and outside-patch export rates (U. Riebesell et al., unpublished manuscript). Although POC export fluxes in the surface layer (50 m) changed from 374 to 1000 $\text{mg C m}^{-2} \text{ d}^{-1}$ with the formation of an iron-induced phytoplankton bloom during SEEDS-1, there was no significant increase in POC export flux measured from the drifting sediment trap deployments at 200 m during the observation period (Aono et al., 2005). These results suggest that most of the POC stayed in the surface mixed layer, that is, did not extend down to 200 m (Takeda and Tsuda, 2005).

For SOFeX-N/S, enhanced POC fluxes out of the mixed layer after iron enrichment were obtained from ^{234}Th observations (SOFeX-S) and free-profiling robotic Lagrangian carbon explorers with transmissometers (SOFeX-N) (Bishop et al., 2004; Buesseler et al., 2005). However, the absolute magnitude of these flux increases was similar to those for natural blooms in the Southern Ocean. During SERIES and SEEDS-2, which allowed comprehensive time-series measurements of the development and decline of an iron-stimulated bloom, POC fluxes defined by the sediment trap deployment showed temporal variation with development and decline phases in the fertilized patch (Boyd et al., 2004; Aramaki et al., 2009). These results suggested that only small part of the decrease in mixed layer POC was subsequently captured by the trap and losses of POC flux were mainly governed by bacterial remineralization and mesozooplankton grazing (Boyd et al., 2004; Tsuda et al., 2007). For SAGE and LOHAFEX under Si limitation in the Southern Ocean (Fig. 4c and 6f), there was no detection for fertilization-induced export by any method (Table 5) (Peloquin et al., 2011; Martin et al., 2013).

In contrast to other previous experiments, EIFEX provided clear evidence that the carbon export was stimulated by

artificial iron addition (Jacquet et al., 2008). During EIFEX, initial the export flux, estimated using ^{234}Th in the upper 100 m of the fertilized patch, was $340 \text{ mg C m}^{-2} \text{ d}^{-1}$ (Fig. 8a and Table 5) (Smetacek et al., 2012). This value remained constant for 25 days after iron addition. Then, between 30 and 36 days after iron addition, a massive increase in export flux as high as $1692 \text{ mg C m}^{-2} \text{ d}^{-1}$ was observed in the fertilized patch, while the initial value remained constant in the unfertilized patch (Fig. 8a and Table 5). The profiling transmissometer with high-resolution coverage also showed that there was an increase in exported POC below 200 m after 28 days. At least half of iron-induced biomass sank far below to a depth of 1000 m with tenfold higher sinking rate (500 m d^{-1}), comparable to the initial conditions, via aggregate formations of diatom species, ‘*Chaetoceros dichaeta*’ (Smetacek et al., 2012). That being said, EIFEX was the exception. Significant changes in export production were not found in any of the other OIF experiments, suggesting that the effectiveness of iron addition on this component of the biological pump remains a question that needs to be resolved in future OIF experiments (Bidigare et al., 1999; Nodder et al., 2001; Boyd et al., 2004; Buesseler et al., 2004; Coale et al., 2004; Aono et al., 2005; Tsuda et al., 2007; Smetacek et al., 2012; Martin et al., 2013).”

2 *The previous OIF differed significantly in experimental design, especially in terms of patch size, duration, location, and also in terms of which measurements were taken. I found the discussion of these aspects in Section 3.2 rather unsatisfying: especially since the authors are in advanced stages of planning a new experiment, what have they concluded from this literature about how best to design an OIF? What are their recommendations in terms of best patch size, minimum duration, and which measurements are required to quantify the effect on carbon sequestration? I think that discussion of these points is important, especially since the authors are clearly interested in persuading the scientific (and, presumably, wider) community that their proposed experiment will provide answers about the scope for geoengineering via OIF. The clear conclusion that they do appear to have drawn is that the experiment should be located inside an eddy. However, to accurately measure downward carbon flux out of the patch at the depth of maximum winter mixing will require a large patch to ensure that sediment traps potentially several hundred metres below the surface are not at too high a risk to actually miss possible particle fluxes. What is their conclusion about the minimum duration that is needed? Given the results of SERIES, SEEDS-2, EIFEX, and LOHAFEX, it would seem to me that one should aim at between 35 and 40 days post-fertilisation. Further, what recommendations can be made about measurement approaches to quantify carbon fluxes? An important point to me is that having multiple redundant methods is very important, e.g. thorium profiles, frequent deployments of sediment traps at multiple depths (ideally neutrally buoyant traps), and high-frequency measurements of properties such as pCO_2 and $\text{O}_2\text{:Ar}$ ratios. It also strikes me that autonomous platforms should play a much greater role in future OIF than they have in the past, e.g. a combination of gliders and Lagrangian floats equipped with biogeochemical sensors. Especially bio-optical sensors such as fluorescence and backscatter can be extremely useful to help constrain downward particle fluxes and their vertical and horizontal variations.*

→ We agree. More discussion is necessary. As suggested by Reviewer, we have moved this Section to “4 Future: Considerations for designing future OIF experiments” to supplement discussion for designing a future OIF experiment that would maximize the effectiveness of OIF. We have revised Section 4 to consider the methods for iron addition (i.e., ‘How’), tracking methods and measurement parameters (i.e., ‘What’), location (i.e., ‘Where’),

timing (i.e., 'When'), and duration (i.e., 'How long') to build on the results of OIF experiments as follows:

- 4 Future: Considerations for designing future OIF experiments (from line 30, page 14 to line 9, page 17):

5 "Scientific research on OIF has focused on improving our understanding of the effectiveness, capacity, and risks of OIF as an atmospheric CO₂ removal strategy. Although the first OIF experiments took place more than twenty years ago, the legal and economic aspects of such a strategy in terms of international laws of the sea and carbon offset markets are not yet clear (ACE CRC, 2015). It is therefore of paramount importance that future OIF experiments continue to focus on the effectiveness and capacity of OIF as a means of reducing of atmospheric CO₂, but in doing so should carefully consider iron addition method (i.e., 'How'), tracking methods and measurement parameters (i.e., 'What'), locations (i.e., 'Where'), timing (i.e., 'When'), and duration (i.e., 'How long') to build
10 on the results of OIF experiments, develop our understanding of the magnitude and sources of uncertainties, and in so doing build confidence in our ability to reproduce results.

How: The first consideration for a successful OIF experiment lies in the strategy/approach to maintain added iron within the upper mixed layer. During the first OIF experiment, IronEx-1, the patch was fertilized with acidified iron(II) sulfate according to the target concentrations of 3.6 nM because iron-enrichment bottle incubation
15 experiments performed in deck-board incubators using ocean water suggested maximum phytoplankton growth rates in response to iron additions of 1–2 nM (Fitzwater et al., 1996). However, subject to horizontal dispersion, concentrations of iron added in the open ocean rapidly decreased from 3.6 nM to 0.25 nM in just four days. Further, the magnitude of the open ocean biogeochemical response was less than bottle enrichment experiments suggested (Coale et al., 1998). Seeking to sustain enhanced iron concentrations in patches, since IronEx-2, the technique of
20 applying repeated (2 to 4) iron infusions has been used in all OIF experiments except SEEDS-1 and FeeP (de Baar et al., 2005; Boyd et al., 2007). Like IronEx-1, SOIREE showed that losses in dissolved iron after the first iron infusion rapidly increased due to horizontal dispersion, and also noted loss due to oxidation of the additional iron(II) to iron(III) (Bowie et al., 2001). However, SOIREE demonstrated that four additions of iron with intervals of about 3 days led to a persistent elevation of both dissolved and particulate iron within the mixed layer at the end of the
25 experiment through fast reduction combined with an increase in the concentration of iron-binding ligands after multiple infusions. Both EIFEX and SOFeX-S also found that multiple iron(II) infusions allowed iron to persist in the mixed layer longer than its expected oxidation times. They determined that the relatively low oxidation rates were related to a combination of photochemical production, slow oxidation, and possibly organic complexation (Croot et al., 2008). Blain et al. (2007) explained that the higher carbon sequestration effectiveness of natural OIF
30 experiments compared to artificial OIF experiments partly resulted from the slow and continuous iron addition that occurs in the natural environment. Short-term infusions of large amounts of iron tend to lead the substantial loss of artificially added iron. Therefore, to increase ration of the amount of carbon flux exported to the amount of iron supplied, multiple additions of iron are more efficient.

What: The second consideration for a successful OIF experiment is effective tracing of fertilized patch including
35 detection of carbon sequestration (Buesseler and Boyd, 2003) and monitoring of possible side effects. OIF side effects include emission of climate-relevant gases such as N₂O and DMS that directly contribute to warming and

cooling of the environment, respectively (Law, 2008). During IronEx-1, the fertilized patch was subsequently traced with large variety of physical-biogeochemical techniques and parameters such as GPS and ARGO equipped drifting buoys, SF₆, Fv/Fm ratio, pCO₂, and chlorophyll fluorescence using underway sampling systems, and satellite images (Martin et al., 1994; Coale et al., 1998). As IronEx-1 provided potential evidence to support Martin's iron hypothesis by showing an increase in phytoplankton bloom with iron enrichment, many subsequent OIF experiments adopted the tracing methods introduced by IronEx-1, and were similarly able to detect environmental changes through the observation of both physical and biogeochemical parameters before and after iron addition (Martin et al., 1994; Coale et al., 1996; Boyd et al., 2000; Tsuda et al., 2005; Coale et al., 2004; Boyd et al., 2004; Smetacek et al., 2012). Carbon export fluxes can be detected using ²³⁴Th, ¹³C_{org}, free-drifting sediment traps, beam-transmissometers, and UVPs (Table 5) (Bidigare et al., 1999; Nodder et al., 2001; Boyd et al., 2004; Buesseler et al., 2004; Coale et al., 2004; Aono et al., 2005; Tsuda et al., 2007; Smetacek et al., 2012; Martin et al., 2013). In particular, it is possible to evaluate the temporal evolution of iron-induced export carbon fluxes into deeper waters by applying the thorium deficiency method and sediment trap fluxes that were used during previous OIF experiments (Table 5). Because of their high vertical resolution, the profiling transmissometer, the UVP with its camera that photographs particles, and transmissometers riding on profiling autonomous floats could provide a record of temporal evolution in POC stocks through successive depth layers once calibrated using POC measurements (Smetacek et al., 2012; Martin et al., 2013). Future OIF experiments could benefit from these technological advances so as to more efficiently trace carbon export flux at higher vertical and temporal resolution than has been done in the past. Nevertheless, the application of multiple methods including trap fluxes and ²³⁴Th deficiency to provide relatively direct flux estimates combined with autonomous profilers with their higher resolution would produce the best results.

Where: The third consideration for a successful OIF experiment is the location selection. The dominance of diatoms in phytoplankton communities plays major role in biological pump efficiency because some species of diatom rapidly sink in aggregate formations and have high accumulation rates of heavily silicified frustules (Tréguer et al., 1995). On the other hand, mesozooplankton (i.e., copepods) graze on large diatoms and so are a major limiting factor in diatom production (Coale et al., 2004; Tsuda et al., 2007). Therefore, to obtain the greatest possible carbon export flux in response to iron addition, OIF experiments should be designed in regions with high silicate concentrations and low copepod abundances. In selecting sites for iron fertilization, it is also important to isolate the iron-fertilized patch from the surrounding unfertilized waters to easily and efficiently observe iron-induced changes (Coale et al., 1996). Ocean eddies provide an excellent setting for OIF experimentation as they have physically rotating water column structures, that naturally tend to isolate interior waters from the surrounding waters. Mesoscale eddies range from 25–250 km in diameter and maintain their characteristics for 10–100 days after formation (Morrow and Le Traon, 2012). Eddy centers, in which fertilization is performed, tend to be subject to relatively slow current speeds compared to the surrounding environment and have high vertical coherence, providing ideal conditions for tracing the same water column from the surface to the deep during the experiment (Smetacek and Naqvi, 2008). Iron additions were carried out at the center of eddies in EisenEx, EIFEX, and LOHAFEX conducted in the Southern Ocean (Smetacek, 2001; Smetacek and Naqvi, 2008; Smetacek and Naqvi, 2010; Smetacek et al., 2012). Observations were also made outside the eddy core well away from the iron-fertilized

patch to provide similar information about environmental conditions to compare with patch observations. EIFEX showed a clear difference in export carbon flux between waters within the patch and external to the patch (Smetacek et al., 2012). Therefore, finding of an appropriate eddy setting in a study area should be one of the high priority considerations in conducting an OIF experiment (Smetacek and Naqvi, 2008).

5 When: The **fourth** consideration for successful OIF experiment **is timing including when an experiment starts**. Primary production in ocean environment is generally limited by nutrient availability and/or by light availability, often referred to as single- or co-limitation. Primary production in the Southern Ocean, a representative HNLC region, is subject to co-limitation by micro-nutrients (i.e., iron) and light availability (Mitchell et al., 1991). Previous Southern Ocean OIF experiments have been conducted from spring to late summer, and revealed that
10 during this time of year primary production is limited by iron supply rather than light availability (de Baar et al., 2005; Smetacek and Naqvi, 2008; Peloquin et al., 2011). **However, the most opportune time, to distinguish phytoplankton blooms increased by iron addition from natural blooms, is during the month of March when natural phytoplankton blooms decline in the Southern Ocean.**

How long: The fifth consideration for successful OIF experiment is how long it lasts. Although it has been reported
15 that the periods that phytoplankton blooms have been maintained by OIF have lasted from ~10 to 40 days (Martin et al., 1994; Coale et al., 1996; Boyd et al., 2000; Tsuda et al., 2005; Coale et al., 2004; Boyd et al., 2004; Smetacek et al., 2012), it has also been suggested that most OIF experiments did not cover the full response times from onset to termination (Boyd et al., 2005). For example, SOIREE and SEEDS-1, had relatively short observation periods (~13 days) and saw increasing trends in primary production throughout the experiments (Fig. 10a), suggesting that
20 the observation period should have been extended. Furthermore, after the end of SOIREE, ocean color satellite images showed continued high chlorophyll-a concentrations (~1 mg m⁻³) in the iron fertilized patch, which was seen as a long ribbon shape that extended some ~150 km for ~46 days; (~7 weeks) after the initial iron addition (Fig. 10b) (Abraham et al., 2000). This result indicates that short experiment periods may not be sufficient for detecting the full influence of artificial iron addition on primary production (Fig. 8b) (Boyd et al., 2000; Tsuda et
25 al., 2003; de Baar et al., 2005). **However, SERIES, SEEDS-2, EIFEX, and LOHAFEX did fully monitor all the phases of the phytoplankton bloom from onset to termination. Among OIF experiments, EIFEX, the second-longest at ~39 days, alone observed iron-induced deep export production between 30 and 36 days after iron addition (Fig. 8a and 10a) (Assmy et al., 2013; Smetacek et al., 2012). Furthermore, long-term observation period covering the later stage of bloom development during natural OIF experiments has made it possible to obtain high carbon sequestration effectiveness (Blain et al., 2007; Pollard et al., 2009).** It is therefore important to predict both the
30 necessary time for onset and the time required for the response to run its full course, otherwise it is not possible to quantify the net effect. **In addition, to detect the enhancement of the carbon export flux to iron addition, the observation period should last at least 35 to 40 days after iron addition.**

In conclusion, to maximize the effectiveness of OIF experiments in the future, we suggest a design that incorporates:
35 **(‘How’) multiple iron additions to 1–2 nM concentration; (‘What’) multiple means of tracing the fertilized patch including both trap fluxes and/or ²³⁴Th deficiency to obtain direct flux estimates and autonomous platforms such as gliders, equipped with biogeochemical sensors, to obtain high vertical resolution, and monitoring side effect**

such as N₂O and DMS; ('Where') in an eddy structure with high silicate concentration and low copepod abundance; ('When') e.g., March in the Southern Ocean; ('How long') at least >~35 days."

3 *The discussion of possible unintended side-effects could be similarly improved by trying to draw clearer conclusions rather than just summarising results from the previous literature. For example, it seems to me that the main conclusion about domoic acid is that it is very variable regardless of fertilisation, with the cited Smith et al. paper actually reporting higher per-cell quotas from natural than from artificially fertilised waters (the cited Trick et al. paper relied on bottle incubations and extrapolations based on claims about likely bloom size made by geoengineering companies on an internet site). Moreover, while a degree of oxygen consumption would certainly result from OIF, the sentence that "Box model solutions have further suggested that anoxic conditions may develop after OIF" is quite misleading: the cited reference is actually a much more realistic 3-dimensional model that only found anoxia developing in part of the western Indian Ocean, and only after many years of sustained complete nutrient utilisation in the Southern Ocean. This is probably a significantly more extreme scenario than could be achieved in practice, suggesting that anoxic conditions are actually quite unlikely. Conversely, increased production of other relevant gases, such as N₂O, is clearly an important concern (though the discussion of DMS could do with some reference to the fact that its role in climate seems to be rather more complex than originally thought).*

→ We apologize for the confusion. Based on the Reviewer's comments, we have provided conclusions about side effects based on recent modeling results and have revised Section "3.1 Environmental side effects" as follows:

- 3.1 Environmental side effects (from line 13, page 11 to line 21, page 13):

"OIF has been proposed as one potential way (*a.k.a.* 'Carbon Capture Storage') of rapidly and efficiently reducing atmospheric CO₂ levels at relatively minimal cost (Buesseler and Boyd, 2003). Over the past 25 years, controlled OIF experiments have illustrated that substantial increases in phytoplankton biomass can be instigated in HNLC regions through iron addition that results in the drawdown of DIC and macronutrients (de Baar et al., 2005; Boyd et al., 2007; Smetacek et al., 2012; Martin et al., 2013). However, the effectiveness of enhancement in this export production, which results in a net transfer of CO₂ from the atmosphere to the ocean intermediate/deep layer (i.e., 'biological pump'), is not yet fully understood or quantified as it appears to vary with region, season, and as yet unknown factors (Smetacek et al., 2012). Therefore, it is uncertain whether OIF has the potential to sequester CO₂ at a significant rate (~1 Gt of CO₂ per year). In the meantime, there are possible environmental side effects in response to iron addition, such as production of greenhouse gases (e.g., N₂O and CH₄) (Lawrence, 2002; Liss et al., 2005; Law, 2008), development of hypoxia/anoxia in water column (Sarmiento and Orr, 1991), and toxic algal blooms (e.g., *Pseudo-nitzschia*) (Silver et al., 2010; Trick et al., 2010), that have been seen and should be addressed before artificial OIF is conducted. These OIF experiment side-effects may themselves effect climate and ecosystem changes that have unexpected negative outcomes (Fuhrman and Capone, 1991). Therefore, it is not surprising that the OIF validation and usefulness has been a subject of debate (Williamson et al., 2012).

OIF experiments have measured climate-relevant gases (i.e., N₂O, CH₄, dimethylsulfide, and halogenated volatile organic compounds) that are produced by biological activity and/or photochemical reaction (Liss et al., 2005) to

investigate change before and after iron addition. CH₄ has been considered to be relatively low risk as most of the CH₄ formed in the ocean is used as energy source for microorganisms and is converted to CO₂ before reaching to the sea surface (Smetacek and Naqvi, 2008; Williamson et al., 2012). Measurements of dissolved CH₄ during the SOFeX-N showed slightly elevated concentrations at less than 1 % (Wingenter et al., 2004). Simulated Southern Ocean large-scale iron fertilization has suggested that enhancement of CH₄ emission would offset only <1 % of the resulting carbon sequestration (Oschlies et al., 2010). On the other hand, the ocean is already a significant source for atmospheric N₂O, which has relatively the long lifetime (~110 years) in the atmosphere and has a global warming potential about 300 times greater than CO₂ (Forster et al., 2007). Therefore, any enhancement of biological production that might enhance N₂O emission could work to increase atmospheric greenhouse gas levels rather than decrease them (Bange, 2006). During the SOIREE experiment, a significant increase (~7 %) in mean N₂O saturation in the pycnocline of the fertilized patch was associated with increased phytoplankton biomass (Law and Ling, 2001). Measurements of N₂O saturation during SERIES also showed increases of 8 % at 30–50 m, which were coincident with the accumulation of ammonium and nitrite attributable to bacterial remineralization (Boyd et al., 2004; Law, 2008). Model estimates suggested that potential N₂O production on longer timescales (6 weeks) would subsequently offset by 6–12 % increased carbon reduction benefits resulting from remineralization of additional carbon fixed during SOIREE (Law and Ling, 2001). This estimate is in the same range as the N₂O offset of 6–18 % suggested by an earlier modeling study (Jin and Gruber, 2003) and the 5–9 % suggested by a more recent modeling study investigating the effectiveness of long-term and large-scale Southern Ocean OIF (Oschlies et al., 2010). Complicating the story, however, excess N₂O was not found after iron addition during EIFEX, which showed significant vertical export with formation of rapidly sinking aggregate (Walter et al., 2005; Law, 2008). An explanation for the absence of N₂O accumulation below EIFEX patch might be limited bacterial remineralization by rapid export to the seafloor (Walter et al., 2005).

Unlike N₂O emissions which have the potential to offset the effectiveness of OIF, dimethylsulfide (DMS), hypothesized to be a precursor of sulfate aerosols that cause cloud formation and so climate cooling, may contribute to the homeostasis of the earth's climate by countering warming from increasing CO₂ (Charlson et al., 1987). The DMS response to iron addition was measured during all OIF experiments. In equatorial Pacific and Southern Ocean, DMS increased, but in the subarctic Pacific, it remained constant or decreased (Lawrence, 2002; Boyd et al., 2007). Significant short-term increases in DMS production were found in IronEx-2, SOIREE, EisenEx, and SOFeX-N (Turner et al., 1996; Turner et al., 2004; Wingenter et al., 2004; Liss et al., 2005). The maximum DMS production observed was a 6.5-fold increase after iron addition during SOIREE (Turner et al., 2004). Similarly, a 5-fold enhancement of DMS was observed during SOFeX-N. Estimates derived by extrapolation of SOFeX-N DMS results to the Southern Ocean OIF experiment with 2 % areas suggested that iron fertilization would enhance DMS production by 20 %, which would lead to a 2 °C decrease in air temperature over the Southern Ocean (Wingenter et al., 2007). Interestingly, there were no significant changes in DMS production after iron addition in SEEDS-1 and SEEDS-2, despite increases in primary production (Turner et al., 1996; Takeda and Tsuda, 2005; Nagao et al., 2009). Contrast to SEEDS-1 and SEEDS-2, DMS production decreased in SERIES experiment due to the relatively high bacterial dimethylsulfoniopropionate (DMSP) metabolism (Levasseur et al., 2006), which is precursor of DMS production. It is therefore clear that there are yet unknown factors affecting iron-induced DMS response, as

it appears that OIF could be a significant source of DMS production in Southern Ocean and yet induce a DMS sink in subarctic Pacific. These results indicate that further observation-based and modeling studies are required to determine different features from place to place (Law, 2008).

Halogenated volatile organic compounds (HVOCs, such as CH₃Cl, CH₃Br, and CH₃I), well known for their ability to destroy ozone in the lower stratospheric ozone and marine boundary layer (Solomon et al., 1994), were also measured during the OIF experiments (Wingenter et al., 2004; Liss et al., 2005). During SOFeX-N experimentation, iron addition results for HVOC were complicated: CH₃Cl concentrations remained unchanged; CH₃Br concentrations increased by ~14 %; and while generally CH₃I concentrations decreased by ~23 % (Wingenter et al., 2004). CH₃I concentrations increased 2-fold in EisenEx (Liss et al., 2005). Therefore, as the DMS response above, further study is needed to understand the complexity of the HVOC response.

Decomposition of iron addition-enhanced biomass may cause decreased oxygen concentrations in the subsurface waters (Williamson et al., 2012). Although mid-water oxygen depletion has not been reported during the OIF experiments to date, it has been suggested that OIF-induced oxygen depletion may occur as increased downward carbon exports elevate microbial respiration (Fuhrman and Capone, 1991). Early studies using box model solutions have further suggested that anoxic conditions may develop after OIF (Sarmiento and Orr, 1991). However, more sophisticated and realistic models associated with OIF-induced oxygen changes in water columns showed well-oxygenated conditions without developing anoxic conditions (Oschlies et al., 2010; Keller et al., 2014).

The changes of phytoplankton community composition after iron addition discussed in Section 2.4 may also have unintended consequences, in particular, toxin production (Silver et al., 2010; Trick et al., 2010). Some OIF experiments (including IronEx-2, SOIRE, EisenEx, and SOFeX-N/S) generated large blooms of diatoms dominated by pennate diatoms belonging to the genus '*Pseudo-nitzschia*' (de Baar et al., 2005; Trick et al., 2010). Some species of the genus '*Pseudo-nitzschia*' have the capacity to produce the neurotoxin domoic acid (DA) that is known to detrimentally affect marine ecosystems. For example, during IronEx-2 and SOFeX-S, high cell abundances of '*Pseudo-nitzschia*' (10⁶ and 10⁵ cells l⁻¹, respectively) combined with moderate DA quotas (0.05 and 1 pg DA cell⁻¹, respectively) produced toxin levels as high as 45 ng DA l⁻¹ in IronEx-2 and 220 ng DA l⁻¹ in SOFeX-S; i.e., toxin levels that is able to cause certain damages to marine communities in coastal waters (Silver et al., 2010). However, no DA was found during EisenEx, even though diatom species of the genus '*Pseudo-nitzschia*' were dominant numerically (Gervais et al., 2002; Assmy et al., 2007).

The direct and indirect environmental consequences of OIF remain unresolved due to inconsistent, highly uncertain outcomes (Williamson et al., 2012; Johnson and Karl, 2002; Chisholm et al., 2001), suggesting that we haven't yet reached to a conclusion as to whether OIF is a feasible carbon removal strategy (Boyd et al., 2007). Therefore, evaluation and prediction are paramount. It continues to be a valuable exercise to seek answers to scientific questions about the effectiveness of OIF as a means of reducing atmospheric CO₂ as well as to quantify possible OIF side effects. In particular, potential trace gas emissions such as N₂O and DMS, which are influenced by the remineralization of sinking particles that follows OIF-induced blooms, are important to understand. They can directly and indirectly modify the desired carbon sequestration effectiveness and they can do so both positively and

negatively. Therefore, monitoring of N₂O and DMS to evaluate the effectiveness of OIF as a geoengineering approach is essential.”

-Specific Comments:

5 **4** *Abstract Line 10, and page 10 final paragraph Line 1: make it clear that these side- effects are possible side effects, and that changes in community composition may have unintended consequences.*

→ We have made it clear by changing “including side effects” to “including possible side effects” in the Abstract (Please refer line 24, page 1) and “The changes of phytoplankton community after iron addition discussed in Section 2.4 also has unintended consequences” to “The changes of phytoplankton community composition after iron addition discussed in Section 2.4 may also have unintended consequences” (Please refer lines 3–4, page 13).

10 **5** *Page 4 Paragraph 3: > and < signs for latitude are the wrong way round.*

→ We corrected “>” and “<” signs for latitude (Please refer lines 21–22, page 4).

6 *Page 12 final paragraph: given the large number and large scale of natural mesoscale blooms in HNLC regions (e.g. due to iceberg-derived iron), I think it is fair to say that the risks to the environment from small-scale OIF experiments is very small indeed, and I think that the authors should be prepared to make that case.*
15 *The risks of large-scale OIF for geoengineering purposes are the risks that are not understood, and small-scale studies are what we therefore need to undertake at this point to assess these risks better.*

→ The reviewer is correct. We have revised Section “3.2 International law of the sea to OIF” by rephrasing sentences as follows:

- 3.2 International law of the sea to OIF (lines 1–8, page 14):

20 “However, this effort has not been able to move forward because we have little knowledge about the potential magnitude of possible side effects related to large-scale geoengineering OIF. It remains difficult to extrapolate findings from the small-scale OIF experiments because the environmental/ecosystem side effects from these miniature studies are themselves quite variable and not yet clearly understood. However, presently available studies do indicate that the known side effects from small-scale studies are themselves small-scale. It therefore seems
25 reasonable that we should continue to undertake small-scale studies to better assess these risks and so lay the groundwork for evaluating the potential efficacy and impacts of large-scale OIF as a geoengineering solution to anthropogenic change.”

7 *Page 14 Paragraph 2: Sentence starting “To data . . .” should read “To date, the only OIF experiment . . .”*

→ Done (Please refer line 17, page 17).

30 **8** *Page 14 Section 4.2.3: What do the authors mean by “rehearsal”? Will they add only a tracer, such as SF6,*

or will iron be added as well?

→ We apologize for the confusion. By “rehearsal”, we intended to indicate that we would conduct hydrographic surveys outside/inside the eddy structure in the eastern Bransfield Basin and employ drifting-buoys without iron addition prior to the actual (eddy structure) OIF experiment. Basically, we would not plan to add SF₆ as a chemical tracer in the KIFES project. We deleted the word and revised the KIFES section (Please refer from line 11, page 17 to line 30, page 19).

9 *Page 14 Section 4.2.4: As I indicated in one of my general comments, I think that future OIF could benefit greatly from using autonomous platforms, such as gliders, equipped with biogeochemical sensors. If this is not planned at present, I would urge the project leaders to consider their use.*

→ Thank you. Yes. We would plan to use autonomous platforms (Please refer line 10, page 19).

10 *Page 15 Section 4.2.5: What is the second stage of KIFES?*

→ We meant the second 5-years of the KIFES project (2021–2025). Given the current status of KIFES funding, we deleted mention of the second stage of KIFES.

11 *In Figure 4, the authors could consider marking the study region proposed for KIFES.*

→ Thank you for your comment. However, we do not mark the study region proposed for KIFES project due to its halt (Please refer the letter at first page of our responses).

12 *Figure 8 provides a summary of carbon flux related data for two experiments, EIFEX and SOIREE (though Fig 8b is referred to in the context of IronEx-2 in the text). Several other experiments did report comparable data, either with sediment traps, thorium deficits, or both. Comparison of these data is obviously complicated by the fact that different experiments measured flux at different depths, but trying to summarise the results of all of the studies that reported particle fluxes might be helpful. Moreover, when the authors state on Page 9 Paragraph 2 that “That being said, EIFEX was the exception. Significant changes in export production were not found in any of the other OIF experiments”, it should be made clear that only a subset of all OIF experiments was actually designed in such a way that an enhancement of downward particle flux could be detected (especially given the short duration of several experiments).*

→ We now compare carbon flux from all the studies in new “Table 5”. Please refer our [Response \(1\)](#).

-General Comments:

13 (1) *The presentation of results from previous experiments seems too much like a catalog of data, but there is no thorough discussion on why the outcomes of the experiments were so different, and what has been learned from these experiments. (2) Further, given that KIFES is planned to take place in the Southern Ocean, it is not obvious to the reader how the detailed presentation of results from experiments carried out in other oceanic basin is relevant here.*

→ (1) We have created a new “Table 2 Summary of OIF experiments; objective, significant results, and limitation” summarizing Section 2 including OIF design, biogeochemical response, and limitations (from line 1, page 32 to line 5, page 33). We have also modified manuscript with new Section “2.6 Significant results and limitations in previous OIF experiments” to discuss why the outcomes of the experiments were so different and what has been learned from these experiments as follows:

- 2.6 Significant results and limitations in previous OIF experiments (from line 32, page 10 to line 10, page 11):

“To understand how various physical and biogeochemical properties response to artificial iron addition in HNLC regions, previous OIF experiments have been conducted with various objectives (Table 2). These various objectives have contributed to develop ideas/approaches to find optimal conditions that have potential capacity to efficiently sequester carbon (Smetacek et al., 2012). To test iron hypothesis, initial artificial OIF experiments (e.g., SEEDS-1 and IronEx-2) have focused on whether iron supply limits phytoplankton growth in HNLC regions and have confirmed increases in phytoplankton biomass by showing maximum drawdown of $p\text{CO}_2$ by 130 ppm in SEEDS-1 and in primary production by $1800 \text{ mg C m}^{-2} \text{ d}^{-1}$ in IronEx-2 (Fig. 7e and f) (de Baar et al., 2005; Boyd et al., 2007). Massive phytoplankton bloom was due to rapid increase in diatom production (Coale et al., 1996; Boyd et al., 2000). There were multiple efforts to detect deep export production from surface iron-induced massive phytoplankton bloom, as the second step of iron hypothesis (Bidigare et al., 1999; Charette and Buesseler, 2000; Coale et al., 2004; Smetacek et al., 2012). EIFEX only showed significant export carbon to deep layer of 3000 m by aggregate formation with highly fast sinking rates (Table 5) (Smetacek et al., 2012). Despite highly increased phytoplankton production in the mixed layer by OIF experiments (e.g., SEEDS-1, SOFeX-N/S, SERIES, and SEEDS-2), export production was relatively low. Thus, the study focus was on high bacterial remineralization (SERIES) and/or grazing pressure (SEEDS-2) in the upper water columns (Boyd et al., 2004; Tsuda et al., 2007). Relatively slight increase in primary production to iron addition ($\sim 500 \text{ mg C m}^{-2} \text{ d}^{-1}$) occurred in SAGE and LOHAFEX experiments, which were designed to investigate biogeochemical responses to iron addition in very low silicate concentrations ($< \sim 2 \text{ nM}$) (Table 2) (Coale et al., 2004; Harvey et al., 2010; Martin et al., 2013).”

→ (2) The reason we are producing a comprehensive review of previous OIF experiments is to lay an efficient groundwork for new projects by determining the advantages and disadvantages, successes, and failures of earlier efforts. We hope that understanding the history of OIF experimentation will lead to more efficient experimental

strategies and designs, which will in turn produce successful OIF experiments through the selection/adoption of useful approaches and tools that have already had verifiable success in the field.

Contrast to the previous experiments, the idea that the KIFES project was developed was initiated from deep-sediment core information obtained in the eastern Bransfield Basin. The paleoclimate team at Korea Polar Research Institute (KOPRI) found geological evidence of intensive organic carbon burial in the sediments (Yoo et al., 2016), which removes atmospheric CO₂, in the eastern Bransfield Basin on the Antarctic Peninsula. The diatomaceous ooze layer was well preserved in the buried sediments of the Bransfield Basin (Bahk et al., 2003; Kang et al., 2003; Bak et al., 2015), and represents the fast sinking of diatoms within a short time. Scientists at KOPRI suspect that enhancement of the diatom flux may be related to input of bioavailable iron that controls phytoplankton population by allowing efficient use of surface nutrients. In addition, this unique increase in diatom production, the fast sinking rate of the organic matter, and the remarkably well preserved organic carbon sediments in this area, suggest the existence of a strong ‘biological pump (i.e., significant export production)’. This type of ‘bottom-up’ approach (see potential for a surface source by looking at the sedimentary evidence) has not been considered in the location selection for previous experiments. Therefore, it is expected that OIF in diatom-dominated eastern Bransfield Basin will be effective for carbon export. Please refer Section “5.1 Background - Bransfield Basin” (Please refer from line 12, page 17 to line 5, page 18).

14 *In the same line of thought, the rationale for artificial vs. natural iron experiments could also be discussed.*

→ Good point. We have added the rationale for artificial vs. natural iron experiment in Section 3.2 as follows:

- 3.2 International law of the sea to OIF (lines 26–30, page 13):

“Nevertheless, as these small-scale OIF experiments have demonstrated considerable potential for easily and efficiently reducing atmospheric CO₂ levels, physical/biogeochemical/ecological models and natural (long-term) iron fertilization experiments have been studied in an effort to overcome some of the limitations of short-term iron-addition experiments and to predict the effectiveness of long-term and large-scale fertilization (Aumont and Bopp, 2006; Blain et al., 2007; Denman, 2008; Pollard et al., 2009).”

- 3.2 International law of the sea to OIF (lines 35–38, page 13):

“Natural OIF experiments also showed much higher carbon sequestration rates than the small-scale OIF experiments (Morris and Charette, 2013), suggesting that there may be scaling or timing issues in the smaller experiments that preclude simple scaling-up as a prediction tool (see discussion in Section 4).”

→ We also have added the rationale for artificial vs. natural iron experiment in Section 4 as follows:

- 4 Future: Considerations for designing future OIF experiments (lines 14–16, page 15):

“Blain et al. (2007) explained that the higher carbon sequestration effectiveness of natural OIF experiments compared to artificial OIF experiments partly resulted from the slow and continuous iron addition that occurs in

the natural environment.”

- 4 Future: Considerations for designing future OIF experiments (from line 40, page 16 to line 1, page 17):

“Furthermore, long-term observation period covering the later stage of bloom development during natural OIF experiments has made it possible to obtain high carbon sequestration effectiveness (Blain et al., 2007; Pollard et al., 2009).”

15 **Overall, model studies are poorly represented in this review. Given that C sequestration estimates, as well as large scale and long term impacts of OIF are mostly determined through model studies, it might be relevant to mention them and how additional experiments might help constrain such models (see also comments below).**

→ Thank you for pointing out this deficiency. We have added the model results for carbon sequestration estimates in Section 3.2 as follows:

- 3.2 International law of the sea to OIF (lines 30–38, page 13):

“Earlier simplistic global biogeochemical models suggested that massive fertilization could draw down atmospheric CO₂ by as much as 107 ppm in 100 years (Joos et al., 1991; Peng and Broecker, 1991; Sarmiento and Orr, 1991; Kurz and Maier-Reimer, 1993). Recent global models with a more realistic ecosystem and biogeochemical cycles predict values closer to 33 ppm drawdown in atmospheric CO₂. These results suggest that the amount of carbon sequestration resulting from OIF would represent only a modest offset, a contribution less than 10 % for the range of IPCC future emissions scenarios (Aumont and Bopp, 2006; Denman, 2008). Natural OIF experiments also showed much higher carbon sequestration rates than the small-scale OIF experiments (Morris and Charette, 2013), suggesting that there may be scaling or timing issues in the smaller experiments that preclude simple scaling-up as a prediction tool (see discussion in Section 4).”

We have also added modelling results in our discussion of side effects in Section 3.1 as follows:

- 3.1 Environmental side effects (lines 33–34, page 11):

“Simulated Southern Ocean large-scale iron fertilization has suggested that enhancement of CH₄ emission would offset only <1 % of the resulting carbon sequestration (Oschlies et al., 2010).”

- 3.1 Environmental side effects (lines 2–7, page 12):

“Model estimates suggested that potential N₂O production on longer timescales (6 weeks) would subsequently offset by 6–12 % increased carbon reduction benefits resulting from remineralization of additional carbon fixed during SOIREE (Law and Ling, 2001). This estimate is in the same range as the N₂O offset of 6–18 % suggested by an earlier modeling study (Jin and Gruber, 2003) and the 5–9 % suggested by a more recent modeling study investigating the effectiveness of long-term and large-scale Southern Ocean OIF (Oschlies et al., 2010).”

- 3.1 Environmental side effects (from line 39, page 12 to line 2, page 13):

“Early studies using box model solutions have further suggested that anoxic conditions may develop after OIF (Sarmiento and Orr, 1991). However, OIF-induced reductions in oxygen concentration based on more sophisticated and realistic models have been smaller resulting in well-oxygenated end-conditions rather than oceanic anoxia (Oschlies et al., 2010; Keller et al., 2014).”

5 -Specific Comments:

16 p. 7, line 28: the authors explain Fv/Fm but the term is used much earlier in the text. I suggest shifting the explanation to the first time Fv/Fm is used. I am also not sure that the description as written is very useful for people outside the field.

→ Done (Please refer lines 29–30, page 6 and line 29, page 7).

10 **17** p.8, lines 16–28: Given the large differences in mixed layer depth between experiments, I would suggest the authors also discuss mixed layer integrated chlorophyll stocks as these better reflect the real biomass built up (i.e. standing stocks accumulated during EIFEX were similar to those for SEEDS even though concentrations were an order of magnitude lower).

15 → Thank you for suggestion. We have added some sentences about integrated chlorophyll stocks in Section 2.4 as follows:

- 2.4 Biogeochemical responses (lines 31–37, page 8):

20 “However, influence of iron addition on the phytoplankton growth covers from surface to euphotic depth as added iron is mixed within the mixed layer by physical processes (Coale et al., 1998). Although maximum chlorophyll-a concentrations during SEEDS-I (~22 mg m⁻³) were much higher than EIFEX (~3.2 mg m⁻³), mixed layer integrated chlorophyll-a concentrations were similar to ~250 mg m⁻². There were distinct differences between mixed layer integrated chlorophyll-a concentration and surface chlorophyll-a concentration. Therefore, during previous OIF experiments, to quantify the exact changes in phytoplankton biomass to iron addition, it would be important to detect the change in integrated primary productions within MLDs.”

18 p.8, line 26: there is a mistake in the sentence (“were appeared at?”), and the message is not clear.

25 → We apologize for this confusion. We have revised the sentences explaining satellite chlorophyll-a concentration images to clearly deliver the message as follows:

- 2.4 Biogeochemical responses (lines 25–30, page 8):

30 “Spatial changes in chlorophyll-a concentration as a result of iron addition were detected in SOFeX-N/S using Sea-viewing Wide Field-of-view Sensor (SeaWiFS) and MODerate resolution Imaging Spectrometer (MODIS) Terra Level-2 chlorophyll-a images. The chlorophyll-a image at ~28 days after iron addition in the SOFeX-N showed a phytoplankton bloom distribution resembling a long thread shape (~1.0 mg m⁻³), while chlorophyll-a image at ~20

days in the SOFeX-S suggested a somewhat broader bloom pattern ($\sim 0.4 \text{ mg m}^{-3}$) (Fig. 7d) (Westberry et al., 2013).”

19 p. 9, line 1: add “the” before “surface”.

→ Done (line 38, page 8).

20 p. 10 lines 17-21: *More recent model studies do not show development of anoxic conditions for large-scale iron fertilization in the Southern Ocean (see for instance Oeschle et al. Biogeosciences, 7, 4017–4035, 2010; Keller et al. Nature Communications, doi: 10.1038/ncomms4304, 2013).*

→ Thanks for the information. We have added more recent model studies in Section 3.1. Please refer our [Response \(3\)](#).

21 p.10, line 36: Change “also has” to “could also have”

→ We have changed “also has” to “may also have” (also refer [Response \(4\)](#) for this revision).

22 p. 11, line 3: Change “even though generally...” to “even though diatom species of the genus *Pseudo-nitzschia* were dominant numerically”.

→ Done (Please refer lines 11–12, page 13).

23 p. 11, lines 20-28: *I feel that the question how is somehow too easily brushed aside. This review could be used to discuss protocols and relevant parameters that should be measured, applied or developed. Not all experiments followed similar protocols, or measured all parameters.*

→ We have modified manuscript. Please refer our [Response \(13\)](#).

24 p.13 lines 23-31: *(1) Can the authors give a reference for the mentioned studies. (2) Further, the rationale for doing the experiment in the Bransfield Basin is not clear.*

→ (1) Thanks. We included references (lines 23–25, page 17).

→ (2) Please find the revised KIFES parts. Please refer our [Response \(13-2\)](#).

25 Table 2: *It would be more useful if the authors provided with initial nutrient and DIC and the delta values (rather than the final concentrations).*

→ Done (lines 1–6, page 34).

26 Figure 3. *I do not understand how oxygen is part of the settling component.*

→ We have removed this path from “Figure 3” (lines 1–2, page 41).

27 Legend Figure 4, line 3: Change “nitrate and silicate were presented” to “nitrate and silicate were plotted”

→ Thank you. Done (line 13, page 37).

[28] *Figure 5 legend: Change to “Picture for iron addition procedure” to “Illustration” or “Photographs of iron the addition procedure. Panels a-e taken during EIFEX and LOHAFEX*

→ Done (line 18, page 37).

5 **[29]** *Figure 5a legend: Change legend: a) Iron (II) sulfate bags*

→ Done (line 18, page 37).

[30] *Figure 5b legend: The photograph shows the funnel where iron and HCl was poured, not the HCl.*

→ Done (line 19, page 37).

10 **[31]** *Figure 5f: I am not sure were this picture was taken (the corresponding web page gives no information) but I find it misleading as the iron mixture is released in much lower quantities than depicted here (compare with the size of the hose in panel d taken during EIFEX) and has a different appearance too. I would recommend removing this panel, unless reliable information of its provenance can be provided.*

→ The figure has been removed (lines 1–2, page 43).

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Ocean Iron Fertilization Experiments: Past–Present–Future looking to a future with~~Introduction to~~ Korean Iron Fertilization Experiment in the Southern Ocean (KIFES) Project

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Abstract. Since the start of the industrial revolution, human activities have caused a rapid increase in atmospheric CO₂ concentrations, which have in turn been cited as the cause of a variety climate changes such as global warming and ocean acidification. Various approaches have been proposed to reduce atmospheric CO₂ concentrations. The 'Martin (or Iron) Hypothesis' suggests that ocean iron fertilization (OIF) should be an efficient method for stimulating the biological pump in iron-limited high nutrient-low chlorophyll regions. To test the Martin hypothesis, a total 13 OIF experiments have been performed since 1990 in the Southern Ocean (7 times), in the subarctic Pacific (3 times), in the equatorial Pacific (twice), and in the subtropical Atlantic (once). These OIF field experiments demonstrated that primary production could be significantly increased after artificial iron addition. However, effectiveness in export production ~~efficiency~~ revealed by the OIF experiments was unexpectedly low compared to production from natural processes in all, except one of the experiments (i.e., the Southern Ocean European Iron Fertilization Experiment, EIFEX). These results, including possible side effects such as N₂O production and hypoxia development, have been scientifically debated amongst those who support and oppose OIF experimentation. In the context of increasing global and political concerns associated with climate change, it is valuable to examine the validity and usefulness of the OIF. We provide a general overview of the OIF experiments conducted over the last 25 years (past), a discussion of OIF debates including possible side effects and international law (present), a suggestion of considerations for
designing future OIF experiments to maximize the effectiveness of OIF (future), and an introduction to the OIF experiment
design guidelines for a future Korean Iron Fertilization Experiment in the Southern Ocean,~~considerations including possible~~
~~side effects (present), and an introduction to the OIF experiment plan currently being designed by Korean oceanographers~~
~~(future).~~

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Keywords: Ocean Iron Fertilization; High-Nutrient and Low-Chlorophyll regions; Biological Pump; Phytoplankton; Iron

1 Introduction

Since the start of the industrial revolution, human activities have caused a rapid increase in atmospheric CO₂ from ~280 ppm (pre-industry) to ~400 ppm (present) (<http://www.esrl.noaa.gov/>), which has in turn led a variety of climate changes such as global warming and ocean acidification (IPCC, 2013) (Fig. 1). As the Anthropocene-climate system has rapidly changed toward the more unpredictable, scientific consensus is that the negative outcomes are a globally urgent issue that should be resolved in a timely manner for the sake of all lives on Earth (IPCC, 1990, 1992, 1995, 2001, 2007, 2013). Various ideas/approaches have been proposed to relieve/resolve the problem of global warming (Matthews, 1996; Lenton and Vaughan, 2009; Vaughan and Lenton, 2011; IPCC, 2014; Leung et al., 2014; Ming et al., 2014), largely based on two categories: (1) reduction of atmospheric CO₂ – ocean fertilization to enhance biological CO₂ uptake and/or direct capture or storage of atmospheric CO₂ through chemically engineered processes, and (2) control of solar radiation – artificial aerosol injection into the atmosphere to augment cloud formation and cloud brightening to elevate albedo (Fig. 2). One of the most attractive methods among the proposed approaches is *ocean fertilization* which targets the drawdown of atmospheric CO₂ by nutrient addition (e.g., iron, nitrogen or phosphorus compounds) to stimulate the phytoplankton growth via the ocean biological pump (ACE [CRC](#), 2015).

The ocean biological pump (*a.k.a.* ‘export production’) is frequently depicted as a process whereby organic matter produced by phytoplankton during photosynthesis in surface waters is quickly transported to intermediate and/or deep waters (Fig. 3a) (Volk and Hoffert, 1985; De La Rocha, 2007). Although efficiency of the biological pump is mainly controlled by the supply of macro-nutrients (i.e., nitrate, phosphate, and silicate) into the euphotic zone leading to new production (Sarmiento and Gruber, 2006), iron acts as an essential micro-nutrient to stimulate the uptake of macro-nutrients for phytoplankton growth (Fig. 3b) (Martin and Fitzwater, 1988; Martin, 1990; Morel and Price, 2003). In the subarctic Pacific, equatorial Pacific, and Southern Ocean, which are well known as high-nutrient and low-chlorophyll (HNLC) regions (Fig. 4a and b), phytoplankton cannot completely utilize the available macro-nutrients (particularly nitrate) during photosynthesis due to a lack of iron. For this reason, primary production in these HNLC regions is relatively low in spite of the availability of nutrients (Fig. 4a and b).

It is thought, based on Arctic/Antarctic ice core analyses, that atmospheric CO₂ (~180 ppm) during the Last Glacial Maximum (LGM; ~20,000 years ago) was much lower than during pre-industrial times (~280 ppm) (Neftel et al., 1982; Barnola et al., 1987; Petit et al., 1999). Over the last 25 years, several hypotheses have been proposed to explain the mechanisms that lowered atmospheric CO₂ level during the LGM (Broecker, 1982; McElroy, 1983; Falkowski, 1997; Broecker and Henderson, 1998; Sigman and Boyle, 2000). One is particularly relevant to modern nutrient cycling in the Southern Ocean. In 1990, Martin hypothesized an LGM mechanism whereby the biological pump was substantially enhanced due to the relief of iron-limitation in HNLC regions, in particular the Southern Ocean, via high dust inputs (Fig. 3b). These dust inputs are generally regarded as one of major natural iron sources fertilizing oceans. He concluded with the now famous and often cited words “*Give me half a tanker of iron, and I will give you the next ice age*” (Martin, 1990). Since Martin’s hypothesis was first published, there has been enormous interest in ocean iron fertilization (OIF) because only a small amount of iron (C:Fe ratios = 100,000:1, Anderson and Morel, 1982) is needed to stimulate a strong phytoplankton response. Therefore, much of the investigative focus has been centered on artificially adding iron to HNLC regions as a means of accelerating the ocean biological pump (ACE [CRC](#), 2008).

To test the Martin’s hypothesis, 2 natural and 13 artificial OIF experiments for scientific study have been performed to date in the subtropical Atlantic, equatorial Pacific, subarctic Pacific, and Southern Ocean (Blain et al., 2007; Pollard et al., 2009; Strong et al., 2009) (Fig. 4a and Table 1). These OIF experiments demonstrated that primary production could be significantly increased after iron addition (de Baar et al., 2005; Boyd et al., 2007). To evaluate whether OIF has potential as a geoengineering strategy for carbon sequestration, not only the amount of carbon fixed by phytoplankton at the ocean surface but also the

amount of carbon sequestered to the deep ocean must be considered in determining the effectiveness of OIF (Buesseler and Boyd, 2003). High export production/carbon sequestration ~~efficiencies-effectiveness~~ were observed from natural OIF experiments in the Southern Ocean near the Kerguelen Plateau and Crozet Islands (Blain et al., 2007; Pollard et al., 2009). However, the artificial OIF experiments showed unexpectedly weak responses compared to natural production in all the experiments (de Baar et al., 2005; Boyd et al., 2007), except one; the Southern Ocean European Iron Fertilization Experiment, EIFEX (Smetacek et al., 2012). These results, which include side effects such as N₂O production and hypoxia development (Fuhrman and Capone, 1991), have been scientifically debated amongst those who support and oppose OIF experimentation (Chisholm et al., 2001; Johnson and Karl, 2002; Lawrence, 2002; Buesseler and Boyd, 2003; Williamson et al., 2012).

In the context of increasing global and political concerns associated with rapid climate change, it is still valuable to examine the validity and usefulness of artificial OIF experimentation as a climate change strategy. Therefore, the purpose of this paper is (1) to provide an overview of the OIF experiments conducted over the last 25 years, (2) to discuss the pros and cons of OIF, including possible side effects and international law, (3) to suggest considerations for designing future OIF experiments with maximum effectiveness, and (4) to introduce design guidelines for future Korean Iron Fertilization Experiment in the Southern Ocean (KIFES) project.

~~,and (3) to introduce the plans for the Korean Iron Fertilization Experiment in the Southern Ocean (KIFES) currently being designed by Korean oceanographers.~~

2 Past: Overview of artificial OIF experiments

This overview of past OIF experimentation begins in Section 2.1 with a presentation of how each of the experiments was designed and why each was performed (Table 2). The unique prior ocean conditions for the various experiments are described in Section 2.2. Tracing ~~the effects of iron addition the OIF effects~~ is described in Section 2.3 and biogeochemical responses to the OIF experiments are presented in Section 2.4. Enhancement of carbon flux was assessed in Section 2.5 and why the outcomes of the experiments were so different and what has been learned from these experiments were discussed in Section 2.6 (Table 2).

2.1 Design/Objective of artificial OIF experiments

A total of 13 artificial OIF experiments have been conducted in the following areas: HNLC (i.e., nitrate >10 µM) regions such as the equatorial Pacific (twice), subarctic Pacific (3 times), and Southern Ocean (7 times), and one low-nutrient and low-chlorophyll (LNLC) (i.e., nitrate <10 µM) region, i.e., the subtropical Atlantic (once) (Table 1, Fig. 4a and b).

2.1.1 OIF in the equatorial Pacific

The first OIF experiment, IronEx-1 (Table 1), was carried out over 10 days in October 1993 in the equatorial Pacific (Martin et al., 1994; Coale et al., 1998). This region, located to the south of the Galapagos Islands, was proposed as an optimal place to perform an OIF experiment because (1) the warm temperatures, high light intensity, and low cloud cover allowed for rapid phytoplankton growth, (2) the relatively large number of research cruises conducted in the region provided sufficient physical and biogeochemical property information, (3) it was easily accessible, and (4) it provided an opportunity to examine the natural relationship between primary production and iron addition (via iron inputs into open-ocean waters via the plumes off the western coast of Galapagos Islands) before artificial OIF experiment (Martin and Chisolm, 1992; Martin et al., 1994).

However, the magnitude of biogeochemical responses in IronEx-1 was not as dramatic as expected (Martin et al., 1994). Three hypotheses were advanced to explain the unexpectedly weak results: (1) the possibility of other unforeseen micro-nutrient (e.g., cadmium and manganese) limitations, (2) the short residence time of bioavailable iron in the experimental surface patch due to unstable water-column structure, and (3) the extremely high grazing stress placed on the patch by zooplankton (Cullen, 1995).

To investigate the unexpected responses revealed in IronEx-1, a second OIF experiment, IronEx-2, was conducted in May 1995 (Coale et al., 1996). The IronEx-2 research cruise occupied generally the same area for a longer period (17 days) providing more time to collect integrated information about the biogeochemical, physiological, and ecological responses to the OIF experiment. IronEx-2 demonstrated that massive phytoplankton blooming associated with OIF in the equatorial Pacific was possible, and it rekindled interest in and stimulated OIF experiments in other HNLC regions (Coale et al., 1996; Bidigare et al., 1999).

2.1.2 OIF in the Southern Ocean

The Southern Ocean, the largest HNLC region in the World Ocean, became the next region selected for OIF experimentation (Frost, 1996) because of its important role in intermediate and deep water formation, which suggested great potential for affecting the carbon sequestration associated with iron addition (Martin, 1990; Sarmiento and Orr, 1991; Cooper et al., 1996; Marshall and Speer, 2012). The Southern Ocean iron release experiment (SOIREE) (Table 1 and Fig. 4a), the first *in situ* OIF experiment performed in the Southern Ocean, took place in February 1999 (13 days) in the Australasian-Pacific sector of the Southern Ocean (Boyd et al., 2000). Iron-induced phytoplankton blooms confirmed that the supply of iron controls primary production in the Southern Ocean. It has also been shown that a model can produce LGM atmospheric CO₂ levels (~200 ppm) using SOIREE results with atmospheric dust flux obtained from the Vostok ice core analysis (Watson et al., 2000). The following year, a second Southern Ocean OIF experiment, EisenEx ('Eisen' is iron in German), was performed in November (23 days) in a closed cyclonic eddy of the Atlantic sector of the Southern Ocean (Smetacek, 2001).

The Southern Ocean exhibits markedly varied silicate concentrations on either side of the Antarctic Polar Front (PF): low silicate concentrations (<5 μM) to the north of the PF (≤61° S) and high silicate concentrations (>60 μM) to the south of the PF (≥61° S) (Fig. 4c). Silicate-requiring diatoms, which are one of the large-sized phytoplankton groups and have an important role in the biological pump, are responsible for ~75 % of the annual primary production in the Southern Ocean (Tréguer et al., 1995). Therefore, silicate availability is an important factor when considering the enhancement of export production via OIF experimentation. As SOIREE and EisenEx were performed to the south of the PF under intermediate silicate concentration (~5–25 μM) conditions (Boyd et al., 2000; Gervais et al., 2002) (Fig. 4c; Fig. 4a for experiment locations), the interaction between silicate availability and iron addition was not clearly verified. To elucidate this issue, two OIF experiments were conducted during January–February of 2002 in two distinct regions: The Southern Ocean iron experiment-north (SOFeX-N) and -south (SOFeX-S) of the PF (Coale et al., 2004; Hiscock and Millero, 2005) (Table 1).

To measure biologically driven gas fluxes (e.g., CO₂, dimethylsulfide, CO, N₂O, N₂, and O₂), the Surface Ocean Lower Atmosphere Study (SOLAS) Air–Sea Gas Exchange (SAGE) experiment was conducted during March–April 2004 (15 days) in HNLC sub-Antarctic waters (under low silicate concentration) between subtropical region and the PF (Harvey et al., 2010; Law et al., 2011) (Fig. 4c).

Early OIF experiments had not clearly shown whether artificial OIF could effectively reduce atmospheric CO₂ levels through enhancement of the biological pump, i.e., rapid transport of surface organic matter to intermediate/deep waters (Boyd et al., 2007), but the results were interesting enough to spur continued efforts. With the aim of confirming that OIF could increase export production, an experiment known as EIFEX was carried out during February–March 2004 in a PF cyclonic

eddy core (Fig. 5). With the intention of finding deep export production, EIFEX was a much longer experiment (39 days), compared to earlier attempts (~21 days) (Smetacek et al., 2012). The Indian and German Atlantic sector iron fertilization experiment (LOHAFEX; ‘Loha’ is iron in Hindi) was conducted during January–March 2009 (40 days) also in a PF cyclonic eddy at the same latitude with EIFEX, but under low silicate concentration (Fig. 4c) again with the aim of investigating an iron fertilized bloom in the surface layer, deep export carbon production, and biomass converted back into CO₂ by bacteria and/or zooplankton (Smetacek and Naqvi, 2010; Martin et al., 2013).

2.1.3 OIF in the subarctic North Pacific

A strong longitudinal gradient in aeolian dust deposition (i.e., high dust deposition in the west to low in the east), known as natural OIF, has been found in the subarctic North Pacific (Duce and Tindale, 1991). However, there was little information about differences in phytoplankton biomass and communities along the longitudinal dust gradient (Duce and Tindale, 1991; Moore et al., 2002). To investigate the relationship between phytoplankton biomass/community and this dust gradient, the Subarctic Pacific iron Experiment for Ecosystem Dynamics Study-1 (SEEDS-1) was conducted in July–August 2001 (13 days) in the western subarctic gyre using the RV *Kaiyo-Maru* (Tsuda et al., 2003, 2005), and the Subarctic Ecosystem Response to Iron Enrichment Study (SERIES) was performed in July–August 2002 (25 days) in the Gulf of Alaska using the RV *John P. Tully*, *El Puma*, and *Kaiyo-Maru* (Boyd et al., 2004, 2005). The main objective of SERIES was to investigate the duration of phytoplankton blooming (i.e., start to finish) after iron addition. Two years later, SEEDS-2 repeated the experiment in almost same location and season with SEEDS-1 using the RV *Hakuho-maru* and *Kilo-Moana* (Tsuda et al., 2007).

2.1.4 OIF in the subtropical North Atlantic

To investigate influence of co-limited iron and phosphate on primary production, the *in situ* PO₄³⁻ and Fe²⁺ addition experiment (FeeP) was conducted by adding both phosphate and iron in LNL region of the subtropical North Atlantic during April–May 2004 (21 days) using two RV *Charles Darwin* and *Poseidon* (Rees et al., 2007).

2.2 Environmental conditions prior to iron addition

To investigate initial environmental conditions (~1–7 days before iron addition), physical and biogeochemical properties were determined at the sites of the OIF experiments (Steinberg et al., 1998; Coale et al., 1998; Bakker et al., 2001; Boyd and Law, 2001; Gervais et al., 2002; Coale et al., 2004; Boyd et al., 2005; Takeda and Tsuda, 2005; Tsuda et al., 2007; Cisewski et al., 2008; Harvey et al., 2010; Cavagna et al., 2011) (Fig. 6, Table 2-3 and 3-4). The OIF experiments were conducted under a wide range of physical conditions in terms of mixed layer depth (MLD) and sea surface temperature (SST).

The MLDs ranged from 10 m (SEEDS-1) to 97.6 m (EIFEX) (Fig. 6c), and were shallower in the equatorial Pacific (mean ± SD = 27.5 ± 2.5 m; SD represents standard deviation) and subarctic Pacific (mean ± SD = 22.7 ± 9.0 m) than in the Atlantic Ocean (FeeP: 40 m) and Southern Ocean (mean ± SD = 56.8 ± 18.9 m). Variation in MLD was highest in the OIF experiments conducted in the Southern Ocean and lowest in those conducted in the equatorial Pacific. MLDs in the experiments performed in the western subarctic Pacific were much shallower in SEEDS-1 (10 m) than in SEEDS-2 (28 m), even though the two experiments were carried out in nearly in the same location and season (Tsuda et al., 2007).

SST at the OIF sites ranged from -0.5 °C (SOFeX-S) to 25.2 °C (IronEx-2) (Fig. 6d). SST was much higher in the OIF experiments conducted in the equatorial Pacific (mean ± SD = 24.1 ± 1.15 °C) and Atlantic Ocean (FeeP: 20.7 °C) than those conducted in the Southern Ocean (mean ± SD = 9.4 ± 2.2 °C) and subarctic Pacific (mean ± SD = 4.9 ± 3.7 °C). Although the

two OIF experiments carried out in the equatorial Pacific occurred in different seasons (i.e., IronEx-1: October, IronEx-2: May), the surface physical conditions were quite similar (Steinberg et al., 1998). SOFeX-N/S which were conducted along the same line of longitude in the Southern Ocean exhibited distinct differences in SST; 7.1 °C in SOFeX-N and -0.5 °C in SOFeX-S (Coale et al., 2004). Among the OIF experiments conducted in the Southern Ocean, SAGE carried out in the late summer (late March – early April) had the highest SST (11.5 °C) (Harvey et al., 2010).

Regions for OIF experimentation have usually been selected using preliminary surveys to confirm that the sites were subject to HNLC conditions: high nitrate concentration ($>10 \mu\text{M}$) and low chlorophyll-a concentration ($<1 \text{ mg m}^{-3}$). Nitrate concentrations ranged from 7.9 μM (SAGE) to 26.3 μM (SOFeX-S) (Fig. 6e and Table 23). Among the various OIF HNLC experiment sites, the equatorial Pacific (i.e., IronEx-1 and IronEx-2) had the lowest initial nitrate concentrations (mean \pm SD = $10.6 \pm 0.2 \mu\text{M}$), while the Southern Ocean had the highest (mean \pm SD = $21.2 \pm 5.8 \mu\text{M}$). One exception to the focus on HNLC study sites was the FeeP experiment which took place in the subtropical North Atlantic, a typically LNLC region (nitrate $<0.01 \mu\text{M}$ and chlorophyll-a $<1 \text{ mg m}^{-3}$) (Fig. 6e and h, Table 23 and 34).

The full range of initial silicate concentrations for all the OIF experiments is expressed in the Southern Ocean where values ranged widely from 0.83 μM (SAGE) to 62.8 μM (SOFeX-S) (Fig. 6f and Table 23). Generally speaking, however, initial silicate concentrations were lower in the equatorial Pacific (mean \pm SD = $4.5 \pm 0.6 \mu\text{M}$) than in the Southern Ocean (mean \pm SD = $15.1 \pm 20.4 \mu\text{M}$) and subarctic Pacific (mean \pm SD = $27.3 \pm 9.6 \mu\text{M}$). Nevertheless, SOFeX-N, SAGE, and LOHAFEX all conducted in the Southern Ocean were representative of very low-silicate HNLC (HNLCLSi) regions with initial silicate concentrations less than 2.5 μM (Coale et al., 2004; Harvey et al., 2010; Martin et al., 2013).

Phosphate concentrations ranged from 0.01 μM (FeeP) to 1.9 μM (SOFeX-S) (Table 23). Consistent with the World Ocean Circulation Experiment sections and maps (Talley et al., 2007; Koltermann et al., 2011) which suggest increasing surface and near surface nitrate values from Antarctica equatorward, initial Southern Ocean phosphate concentrations were higher to the south 50° S (mean \pm SD = $1.6 \pm 0.2 \mu\text{M}$) than to the north (mean \pm SD = $1.1 \pm 0.4 \mu\text{M}$). They were also higher in the Atlantic sector (mean \pm SD = $1.6 \pm 0.2 \mu\text{M}$) than in the Pacific sector (mean \pm SD = $1.0 \pm 0.5 \mu\text{M}$). Consistent with both the meridional gradient and the basin differences, IronEx in the equatorial Pacific found generally lower initial phosphate values ($<1 \mu\text{M}$) similar to those seen by SAGE in the southwest Pacific.

Using continuous shipboard measurement systems, OIF experiments have also observed initial surface partial pressure of CO₂ ($p\text{CO}_2$) conditions (Wanninkhof and Thoning, 1993; Steinberg et al., 1998; Bakker et al., 2001; Bakker et al., 2005; Hiscock and Millero, 2005; Takeda and Tsuda, 2005; Smetacek et al., 2005; Wong et al., 2006; Tsumune et al., 2009; Currie et al., 2011). Initial $p\text{CO}_2$ values ranged from 330 ppm (SAGE) to 538 ppm (IronEx-2) (Table 23). Initial $p\text{CO}_2$ values were much higher in the equatorial Pacific (mean \pm SD = $504.5 \pm 33.5 \text{ ppm}$) than those in the Southern Ocean (mean \pm SD = $355.3 \pm 12.5 \text{ ppm}$) and subarctic Pacific (mean \pm SD = $370 \pm 16.3 \text{ ppm}$).

As previously mentioned, photosynthetic quantum efficiency (F_v/F_m , where F_m is the maximum chlorophyll fluorescence yield and F_v is the difference between F_m and the minimum chlorophyll fluorescence yield) the F_v/F_m ratio, a measure of the photosynthetic efficiency of phytoplankton, is widely used to determine the degree to which iron is the limiting nutrient for phytoplankton growth (F_v/F_m ranges from 0 to 1 where conditions are less iron limited condition as F_v/F_m approaches 1) (Boyd et al., 2005). Initial F_v/F_m ratios were less than ~ 0.3 (Fig. 6g and Table 34) suggesting a tendency for iron limitation. Prior to iron addition, initial chlorophyll-a concentration, measured by fluorometer, ranged from 0.04 mg m^{-3} (FeeP) to 0.9 mg m^{-3} (SEEDS-1) (Fig. 6h and Table 34). However, as was the case for nitrate, compared to all the other OIF experiment sites, FeeP showed unusually low initial chlorophyll-a. The average initial OIF chlorophyll-a concentration was $0.43 \pm 0.27 \text{ mg m}^{-3}$. Prior to the OIF experiments, except in SEEDS-1, SOFeX-S, and EIFEX where the diatoms were dominated by micro-plankton (20–200 μm), phytoplankton communities were dominated by pico-plankton (0.2–2.0 μm) and

nano-plankton (2.0–20 μm) (Coale et al., 1998; Landry et al., 2000; Boyd and Law, 2001; Gervais et al., 2002; Tsuda et al., 2005; Coale et al., 2004; Boyd et al., 2005; Hoffmann et al., 2006; Harvey et al., 2010; Tsuda et al., 2007; Martin et al., 2013).

2.3 Tracing the effects of iron addition

Iron(II) and sulfate aerosols are ubiquitous in the atmosphere, and therefore iron-sulfate ($\text{FeSO}_4 \cdot \text{H}_2\text{O}$), a common form of combined iron that enters the ocean environment via dust deposition, has been frequently regarded as a bioavailable iron source for glacial periods (Zhuang et al., 1992; Zhuang and Duce, 1993; Spolaor et al., 2013). In addition, iron-sulfate is a common inexpensive agricultural fertilizer that is relatively soluble in acidified seawater (Coale et al., 1998). Therefore, OIF experiments have been carried out by releasing commercial iron-sulfate dissolved in acidified seawaters into moving ship propeller wash (Fig. 5).

The patch size fertilized by the first iron addition varied from 25 km^2 (e.g., FeeP; iron addition of 1840 kg) to 300 km^2 (e.g., LOHAFEX; iron addition of 2000 kg) (Boyd et al., 2007; Martin et al., 2013) (Table 1 and Fig. 6a and b). In general, background dissolved iron concentrations in the ocean environment are <0.2 nM. During the OIF experiments, dissolved iron concentrations increased to ~ 1.0 – 4.0 nM and decreased to background concentrations within days (Table 1). The fast decrease in dissolved iron concentrations indicates that iron-sulfate was transformed chemically into a solid form that readily sticks to other substances. This process occurs more rapidly in warmer waters (ACE [CRC](#), 2015). Therefore, except for the single iron addition experiments of IronEx I, SEEDS-1, and FeeP (Martin et al., 1994; Tsuda et al., 2005; Rees et al., 2007), to maintain an iron-fertilized patch, most of the OIF experiments conducted multiple iron additions at the patch centre. These multiple addition experiments included: (2 additions) EIFEX, SERIES, SEEDS-2, LOHAFEX (Boyd et al., 2005; Smetacek et al., 2012; Martin et al., 2013), (3 additions) IronEx-2, EisenEx, SOFeX-N (Coale et al., 1996; Gervais et al., 2002; Coale et al., 2004; Nishioka et al., 2005), and (4 additions) SOIREE, SOFeX-S, SAGE (Boyd and Law, 2001; Coale et al., 2004; Harvey et al., 2010) (Table 1).

To trace the iron-fertilized patch, OIF experiments used a combination of biogeochemical-based and physical-based approaches. In biogeochemical approaches, the OIF experiments (except EIFEX) used sulfur hexafluoride (SF_6) artificially added as a chemical tracer (Martin et al., 1994; de Baar et al., 2005). SF_6 is useful for investigating physical mixing and advection-diffusion processes in the ocean environment due to its low solubility, nontoxicity, and biogeochemically inert characteristics (Law et al., 1998). Injected SF_6 concentrations were continuously monitored using gas chromatography with an electron capture detector system (Law et al., 1998; Tsumune et al., 2005). Usually only one SF_6 injection was necessary as background levels are generally extremely low in the ocean (<1.2 fM; f: femto-, 10^{-15}) (Law et al., 1998; Law et al., 2006; Martin et al., 2013), however, in the SAGE experiment with higher mixing and lateral dilution, there were three injections (Harvey et al., 2010). Underway sampling systems, measuring biogeochemical parameters such as [Fv/Fm ratio](#)~~photosynthetic quantum efficiency (Fv/Fm, where Fm is the maximum chlorophyll fluorescence yield and Fv is the difference between Fm and the minimum chlorophyll fluorescence yield)~~, $p\text{CO}_2$, and chlorophyll fluorescence, were also used in the fertilized patch as alternative means of following the patch (Gervais et al., 2002; Boyd et al., 2005; Tsuda et al., 2007; Harvey et al., 2010; Smetacek et al., 2012).

In physically based approaches, surface-drifting buoys equipped with Array for Real-time Geostrophic Oceanography (ARGO) and Global Positioning System (GPS) sensors have been used to map moving fertilized patches in space and time (Coale et al., 1998; Boyd and Law, 2001; Law et al., 2006; Martin et al., 2013). Buoy position can be transmitted to the ship every 5–10 min. The NASA-airborne oceanographic lidar aircraft have also been employed to assess the large-scale effects of

iron addition on surface chlorophyll in the fertilized patch compared to surrounding regions (Martin et al., 1994).

2.4 Biogeochemical responses

The biogeochemical responses to a wide range of iron addition (350–4000 kg) via OIF experiments in the HNLC regions were surveyed over periods ranging from 10–40 days (Table 1 and Fig. 6b). The initial response was a rapid increase of Fv/Fm ratio generally observed within the first 24 hours after iron addition. This was not the case in SEEDS-1 and SEEDS-2 where a detectable increase was observed 3–5 days later. The maximum post-iron-addition Fv/Fm ranged from 0.31 (SEEDS-1) to 0.65 (SOIRE and SOFeX-S) and Fv/Fm generally reached values of 0.5 or greater (Table 43 and Fig. 7a). The increase in Fv/Fm ratio after iron addition suggests that phytoplankton response to iron enrichment is prompt, and results support the hypothesis that natural phytoplankton growth in these HNLC regions is iron-limited (Boyd and Abraham, 2001; Gervais et al., 2002; Tsuda et al., 2003; Boyd et al., 2005; Barber and Hiscock, 2006; Tsuda et al., 2007; Peloquin et al., 2011; Croot et al., 2008; Martin et al., 2013).

Depletion of macro-nutrients in fertilized patches provides indirect evidence that phytoplankton growth in surface waters is driven by iron fertilization (Boyd and Law, 2001). Significant nitrate uptake (i.e., $\Delta\text{Nitrate} = [\text{NO}_3^-]_{\text{post-fertilization}} - [\text{NO}_3^-]_{\text{pre-fertilization}} < 0$) occurred in all the OIF experiments, except SAGE (Table 23 and Fig. 7b) (Martin et al., 1994; Boyd et al., 2000; Hiscock and Millero, 2005; Law et al., 2011). Negative $\Delta\text{Nitrate}$ ranged from $-0.7 \mu\text{M}$ in the equatorial IronEx1 experiment to $-15.8 \mu\text{M}$ in SEEDS-1. However, in SAGE, concentrations of macro-nutrients in the iron fertilized patch exceeded the initial concentrations (i.e., $\Delta\text{Nitrate} > 0$) due to the physical processes such as deepened ~~mixed layer depth~~MLD and lateral advection of high nutrient waters (Table 23 and Fig. 7b) (Law et al., 2011).

Changes in surface water chlorophyll-a concentrations are a direct indication of the effect of iron addition on phytoplankton growth (Fig. 7c). Generally, chlorophyll-a concentrations increased substantially 2- to 20-fold with max values of $\sim 0.1 \text{ mg m}^{-3}$ (FeeP) to 22 mg m^{-3} (SEEDS-1) (Fig. 7c and Table 34) when nitrate concentrations sharply decreased from 3–5 days after iron addition (Tsuda et al., 2003; Coale et al., 2004; Boyd et al., 2004; Tsuda et al., 2007; Peloquin et al., 2011; Smetacek et al., 2012). SEEDS-1 and SEEDS-2, performed under similar conditions, presented similar initial chlorophyll-a concentrations (0.8 mg m^{-3}), but their responses to iron addition were different. Iron-stimulated max chlorophyll-a concentration in SEEDS-2 ($\sim 2.5 \text{ mg m}^{-3}$) was much lower than those of SEEDS-1 ($\sim 22 \text{ mg m}^{-3}$) (Tsuda et al., 2007). Satellite observations were used to spatially and temporally map OIF phytoplankton response (Boyd et al., 2000; Coale et al., 2004; Boyd et al., 2005; Westberry et al., 2013). Spatial changes in chlorophyll-a concentration as a result of iron addition were detected in SOFeX-N/S using Sea-viewing Wide Field-of-view Sensor (SeaWiFS) and MODerate resolution Imaging Spectrometer (MODIS) Terra Level-2 chlorophyll-a images. The chlorophyll-a image at ~ 28 days after iron addition in the SOFeX-N showed a phytoplankton bloom distribution resembling a long thread shape ($\sim 1.0 \text{ mg m}^{-3}$), while chlorophyll-a image at ~ 20 days in the SOFeX-S suggested a somewhat broader bloom pattern ($\sim 0.4 \text{ mg m}^{-3}$) (Fig. 7d) (Westberry et al., 2013). ~~Sea-viewing Wide Field-of-view Sensor (SeaWiFS) and MODerate resolution Imaging Spectrometer (MODIS) Terra Level 2 chlorophyll-a images showed that increased chlorophyll-a concentrations after iron addition were appeared at ~ 28 days after iron addition in the SOFeX-N with a long thread shape (1.0 mg m^{-3}) and at ~ 20 days in the SOFeX-S over somewhat broad area (0.4 mg m^{-3}) (Fig. 7d) (Westberry et al., 2013).~~

However, influence of iron addition on the phytoplankton growth covers from surface to euphotic depth as added iron is mixed within the mixed layer by physical processes (Coale et al., 1998). Although maximum chlorophyll-a concentrations

during SEEDS-1 ($\sim 22 \text{ mg m}^{-3}$) were much higher than EIFEX ($\sim 3.2 \text{ mg m}^{-3}$), mixed layer integrated chlorophyll-a concentrations were similar to $\sim 250 \text{ mg m}^{-2}$. There were distinct differences between mixed layer integrated chlorophyll-a concentration and surface chlorophyll-a concentration. Therefore, during previous OIF experiments, to quantify the exact changes in phytoplankton biomass to iron addition, it would be important to detect the change in integrated primary productions within MLDs. Associated with the OIF-induced phytoplankton blooms, the magnitude of primary productivity integrated from the surface to euphotic depth in iron fertilized patches also became significantly elevated compared to initial levels (i.e., $\Delta \text{PP} = \text{PP}_{\text{post-fertilization}} - \text{PP}_{\text{pre-fertilization}}$, where PP is primary productivity). Increases in ΔPP ranged from $360 \text{ mg C m}^{-2} \text{ d}^{-1}$ (SAGE) to $1800 \text{ mg C m}^{-2} \text{ d}^{-1}$ (IronEx-2) with maximum values of $790 \text{ mg C m}^{-2} \text{ d}^{-1}$ (EisenEx) to $2430 \text{ mg C m}^{-2} \text{ d}^{-1}$ (IronEx-2) (Fig. 7e and Table 4). As a result of increased ΔPP , drawdown of $p\text{CO}_2$ (negative $\Delta p\text{CO}_2$: air \rightarrow sea) was enhanced during the all OIF experiments except SAGE (Fig. 7f). In SAGE, physical mixing caused an increase in macro-nutrients (positive $\Delta \text{Nitrate}$, Fig. 7b), which resulted in a reversed $p\text{CO}_2$ pattern (positive $\Delta p\text{CO}_2$: sea \rightarrow air) (Currie et al., 2011). The largest $\Delta p\text{CO}_2$ change occurred in SEEDS-1 conducted in the subarctic North Pacific (Fig. 7f). It also produced the largest $\Delta \text{Nitrate}$ and the greatest chlorophyll increase (Fig. 7b and c) (Tsuda et al., 2003; de Baar et al., 2005). Overall, OIF $\Delta p\text{CO}_2$ reductions ranged from -6 ppm (SEEDS-2) to -130 ppm (SEEDS-1) (Table 3 and Fig. 7f), and were associated with DIC decreases of $6 \text{ }\mu\text{M}$ (IronEx-1) to $58 \text{ }\mu\text{M}$ (SEEDS-1) (Steinberg et al., 1998; Bakker et al., 2001; Bakker et al., 2005; Boyd et al., 2007; Berg et al., 2011; Currie et al., 2011).

Using both microscopes and high performance liquid chromatography pigment analysis, changes in phytoplankton community effected by iron addition were also investigated. During IronEx-2, SOIREE, EisenEx, SEEDS-1, SOFeX-S, SERIES, and EIFEX, the dominant phytoplankton community tended to shift from pico- and nano-plankton to micro-plankton, resulting in diatom-dominated phytoplankton blooming, a key component for biological pump enhancement (Landry et al., 2000; Boyd and Law, 2001; Gervais et al., 2002; Tsuda et al., 2005; Coale et al., 2004; Boyd et al., 2005; Hoffmann et al., 2006; Harvey et al., 2010). However, there were no observations on taxonomic shift toward diatom-dominated phytoplankton communities in other OIF experiments (Coale et al., 1998; Coale et al., 2004; Rees et al., 2007; Tsuda et al., 2007; Peloquin et al., 2011; Martin et al., 2013). As noted above, the SEEDS-1 and SEEDS-2 experiments were carried out under similar ocean conditions. Nevertheless, SEEDS-2, which resulted in a minimal increase in chlorophyll-a ($< 3 \text{ mg m}^{-3}$), was also subject to extensive copepod (meso-zooplankton; $200\text{--}2000 \text{ }\mu\text{m}$) grazing (~ 5 times greater than in SEEDS-1) and therefore did not produce a prominent diatom bloom (Tsuda et al., 2007).

~~Associated with the OIF induced phytoplankton blooms, the magnitude of primary productivity integrated from surface to euphotic depth in iron fertilized patches also became significantly elevated compared to initial levels (i.e., $\Delta \text{PP} = \text{PP}_{\text{post-fertilization}} - \text{PP}_{\text{pre-fertilization}}$, where PP is primary productivity). Increases in ΔPP ranged from $360 \text{ mg C m}^{-2} \text{ d}^{-1}$ (SAGE) to $1800 \text{ mg C m}^{-2} \text{ d}^{-1}$ (IronEx 2) with maximum values of $790 \text{ mg C m}^{-2} \text{ d}^{-1}$ (EisenEx) to $2430 \text{ mg C m}^{-2} \text{ d}^{-1}$ (IronEx 2) (Fig. 7e and Table 3). As a result of increased ΔPP , drawdown of $p\text{CO}_2$ (negative $\Delta p\text{CO}_2$: air \rightarrow sea) was enhanced during the all OIF experiments except SAGE (Fig. 7f). In SAGE, physical mixing caused an increase in macro nutrients (positive $\Delta \text{Nitrate}$, Fig. 7b), which resulted in a reversed $p\text{CO}_2$ pattern (positive $\Delta p\text{CO}_2$: sea \rightarrow air) (Currie et al., 2011). The largest $\Delta p\text{CO}_2$ change occurred in SEEDS 1 conducted in the subarctic North Pacific. It also produced the largest $\Delta \text{Nitrate}$ and the greatest chlorophyll increase (Fig. 7f) (Tsuda et al., 2003; de Baar et al., 2005). Overall, OIF $\Delta p\text{CO}_2$ reductions ranged from -6 ppm (SEEDS 2) to -130 ppm (SEEDS 1) (Table 2 and Fig. 7f), and were associated with DIC decreases of $6 \text{ }\mu\text{M}$ (IronEx 1) to $58 \text{ }\mu\text{M}$ (SEEDS 1) (Steinberg et al., 1998; Bakker et al., 2001; Bakker et al., 2005; Boyd et al., 2007; Berg et al., 2011; Currie et al., 2011).~~

2.5 Assessment of export carbon flux

Early OIF experiments showed that iron addition stimulates the first step of the biological pump, promotion of phytoplankton growth. To determine whether the second step of the biological pump, export of carbon to the deep sea (i.e., increased export production), is enhanced after iron addition, the export flux of particulate organic carbon (POC) has been estimated using, either together and/or individually, chemical tracers such as natural radiotracer thorium-234 (^{234}Th ; half-life = 24.1 days) and the stable carbon isotope of particulate organic matter ($^{13}\text{C}_{\text{org}}$), free-drifting sediment traps, beam-transmissometers, and underwater video profilers (UVP) (Table 5) (Bidigare et al., 1999; Nodder et al., 2001; Boyd et al., 2004; Buesseler et al., 2004; Coale et al., 2004; Aono et al., 2005; Tsuda et al., 2007; Smetacek et al., 2012; Martin et al., 2013).

The ^{234}Th isotope has a strong affinity for suspended particles, and the extent of ^{234}Th removal in the water column is indicative of the export production below the euphotic zone associated with surface primary productivity (Buesseler, 1998). In IronEx-2, which was the first OIF experiment in which POC flux was estimated, surface values were calculated from the so-called ^{234}Th activity balance method (Bidigare et al., 1999). The ^{234}Th deficiency of the surface ocean (25 m) during IronEx-2 was evident in the iron-fertilized patch, indicating iron-stimulated export production (Table 5). However, there were no ^{234}Th observations conducted in the unfertilized patch for comparison and nor were there observations to estimate downward POC export to the deep ocean (Bidigare et al., 1999).

SOIREE was first study to quantify downward export processes to the deep Southern Ocean using a comprehensive suite of methods such as ^{234}Th and $^{13}\text{C}_{\text{org}}$ estimates derived from high volume pump sampling, free-drifting sediment trap deployments, and beam transmissometer (Nodder and Waite, 2001). However, no measurable change in carbon export was observed in response to iron-stimulated primary production during the 13-day occupation of the SOIREE (Fig. 8b and Table 5) (Charette and Buesseler, 2000; Nodder and Waite, 2001; Trull and Armand, 2001; Waite and Nodder, 2001). For EisenEx, ^{234}Th observations showed no differences between in-patch and outside-patch export rates (U. Riebesell et al., unpublished manuscript). Although POC export fluxes in the surface layer (50 m) changed from 374 to 1000 $\text{mg C m}^{-2} \text{d}^{-1}$ with the formation of an iron-induced phytoplankton bloom during SEEDS-1, there was no significant increase in POC export flux measured from the drifting sediment trap deployments at 200 m during the observation period (Aono et al., 2005). These results suggest that most of the POC stayed in the surface mixed layer, that is, did not extend down to 200 m (Takeda and Tsuda, 2005).

For SOFeX-N/S, enhanced POC fluxes out of the mixed layer after iron enrichment were obtained from ^{234}Th observations (SOFeX-S) and free-profiling robotic Lagrangian carbon explorers with transmissometers (SOFeX-N) (Bishop et al., 2004; Buesseler et al., 2005). However, the absolute magnitude of these flux increases was similar to those for natural blooms in the Southern Ocean. During SERIES and SEEDS-2, which allowed comprehensive time-series measurements of the development and decline of an iron-stimulated bloom, POC fluxes defined by the sediment trap deployment showed temporal variation with development and decline phases in the fertilized patch (Boyd et al., 2004; Aramaki et al., 2009). These results suggested that only small part of the decrease in mixed layer POC was subsequently captured by the trap and losses of POC flux were mainly governed by bacterial remineralization and mesozooplankton grazing (Boyd et al., 2004; Tsuda et al., 2007). For SAGE and LOHAFEX under Si limitation in the Southern Ocean (Fig. 4c and 6f), there was no detection for fertilization-induced export by any method (Table 5) (Peloquin et al., 2011; Martin et al., 2013).

In contrast to other previous experiments, EIFEX provided clear evidence that the carbon export was stimulated by artificial iron addition (Jacquet et al., 2008). During EIFEX, initial the export flux, estimated using ^{234}Th in the upper 100 m of the fertilized patch, was 340 $\text{mg C m}^{-2} \text{d}^{-1}$ (Fig. 8a and Table 5) (Smetacek et al., 2012). This value remained constant for 25 days after iron addition. Then, between 30 and 36 days after iron addition, a massive increase in export flux as high as 1692 $\text{mg C m}^{-2} \text{d}^{-1}$ was observed in the fertilized patch, while the initial value remained constant in the unfertilized patch (Fig. 8a and Table 5). The profiling transmissometer with high-resolution coverage also showed that there was an increase in exported

POC below 200 m after 28 days. At least half of iron-induced biomass sank far below to a depth of 1000 m with tenfold higher sinking rate (500 m d^{-1}), comparable to the initial conditions, via aggregate formations of diatom species, '*Chaetoceros dichæta*' (Smetacek et al., 2012). That being said, EIFEX was the exception. Significant changes in export production were not found in any of the other OIF experiments, suggesting that the effectiveness of iron addition on this component of the biological pump remains a question that needs to be resolved in future OIF experiments (Bidigare et al., 1999; Nodder et al., 2001; Boyd et al., 2004; Buesseler et al., 2004; Coale et al., 2004; Aono et al., 2005; Tsuda et al., 2007; Smetacek et al., 2012; Martin et al., 2013).

2.6 Significant results and limitations in previous OIF experiments

To understand how various physical and biogeochemical properties response to artificial iron addition in HNLC regions, previous OIF experiments have been conducted with various objectives (Table 2). These various objectives have contributed to develop ideas/approaches to find optimal conditions that have potential capacity to efficiently sequester carbon (Smetacek et al., 2012). To test iron hypothesis, initial artificial OIF experiments (e.g., SEEDS-1 and IronEx-2) have focused on whether iron supply limits phytoplankton growth in HNLC regions and have confirmed increases in phytoplankton biomass by showing maximum drawdown of $p\text{CO}_2$ by 130 ppm in SEEDS-1 and in primary production by $1800 \text{ mg C m}^{-2} \text{ d}^{-1}$ in IronEx-2 (Fig. 7e and f) (de Baar et al., 2005; Boyd et al., 2007). Massive phytoplankton bloom was due to rapid increase in diatom production (Coale et al., 1996; Boyd et al., 2000). There were multiple efforts to detect deep export production from surface iron-induced massive phytoplankton bloom, as the second step of iron hypothesis (Bidigare et al., 1999; Charette and Buesseler, 2000; Coale et al., 2004; Smetacek et al., 2012). EIFEX only showed significant export carbon to deep layer of 3000 m by aggregate formation with highly fast sinking rates (Table 5) (Smetacek et al., 2012). Despite highly increased phytoplankton production in the mixed layer by OIF experiments (e.g., SEEDS-1, SOFeX-N/S, SERIES, and SEEDS-2), export production was relatively low. Thus, the study focus was on high bacterial remineralization (SERIES) and/or grazing pressure (SEEDS-2) in the upper water columns (Boyd et al., 2004; Tsuda et al., 2007). Relatively slight increase in primary production to iron addition ($\sim 500 \text{ mg C m}^{-2} \text{ d}^{-1}$) occurred in SAGE and LOHAFEX experiments, which were designed to investigate biogeochemical response to iron addition in very low silicate concentrations ($< \sim 2 \text{ nM}$) (Table 2) (Coale et al., 2004; Harvey et al., 2010; Martin et al., 2013).

Early OIF experiments showed that iron addition stimulates the first step of biological pump, promotion of phytoplankton growth. To determine whether the second step of biological pump, export of carbon to the deep sea (i.e., increased export production), is enhanced after iron addition, sediment trap and chemical tracers such as natural radiotracer thorium 234 (^{234}Th ; half life = 24.1 days) have been used together and/or individually to estimate the export flux of particulate organic carbon (Bidigare et al., 1999; Nodder et al., 2001; Boyd et al., 2004; Buesseler et al., 2004; Coale et al., 2004; Aono et al., 2005; Tsuda et al., 2007; Smetacek et al., 2012; Martin et al., 2013). ^{234}Th has a strong affinity for suspended particles, and the extent of ^{234}Th removal in the water column is indicative of the export production below the euphotic zone associated with surface primary productivity (Buesseler, 1998). During IronEx 2, ^{234}Th deficiency was evident in the iron fertilized patch indicating iron stimulated export production, however there were no ^{234}Th observations conducted in as unfertilized patch for comparison (Bidigare et al., 1999) (Fig. 8b). During EIFEX, initial export flux estimated using ^{234}Th in the upper 100 m of the fertilized patch was $340 \text{ mg C m}^{-2} \text{ d}^{-1}$. This value remained constant for 25 days after iron addition (Fig. 8a). Then, between 30 and 36 days after iron addition, a massive increase of export flux as high as $1692 \text{ mg C m}^{-2} \text{ d}^{-1}$ was observed in the fertilized patch, while the initial value remained constant in the unfertilized patch (Smetacek et al., 2012). That being said, EIFEX was the exception. Significant changes in export production were not found in any of the other OIF experiments, suggesting that

~~the effect of iron addition on this component of the biological pump remains a question that needs to be resolved possibly by future OIF experimentation (Bidigare et al., 1999; Nodder et al., 2001; Boyd et al., 2004; Buesseler et al., 2004; Coale et al., 2004; Aono et al., 2005; Tsuda et al., 2007; Smetacek et al., 2012; Martin et al., 2013).~~

5 3 Present: OIF debates and considerations including possible side effects and international law

3.1 Environmental side effects

OIF has been proposed as one potential way (*a.k.a.* ‘Carbon Capture Storage’) of rapidly and efficiently reducing atmospheric CO₂ levels at relatively minimal cost (Buesseler and Boyd, 2003). Over the past 25 years, controlled OIF experiments have illustrated that substantial increases in phytoplankton biomass can be instigated in HNLC regions through iron addition that results in the drawdown of DIC and macronutrients (de Baar et al., 2005; Boyd et al., 2007; Smetacek et al., 2012; Martin et al., 2013). However, the effectiveness of enhancement in this export production, which results in a net transfer of CO₂ from the atmosphere to the ocean intermediate/deep layer (*i.e.*, ‘biological pump’), is not yet fully understood or quantified as it appears to vary with region, season, and, as yet unknown factors (Smetacek et al., 2012). Therefore, it is uncertain whether OIF has the potential to sequester CO₂ at a significant rate (~1 Gt of CO₂ per year). In the meantime, there are possible environmental side effects in response to iron addition, such as production of greenhouse gases (*e.g.*, N₂O and CH₄) (Lawrence, 2002; Liss et al., 2005; Law, 2008), development of hypoxia/anoxia in water column (Sarmiento and Orr, 1991), and toxic algal blooms (*e.g.*, *Pseudo-nitzschia*) (Silver et al., 2010; Trick et al., 2010), that have been seen and should be addressed before artificial OIF is conducted. These OIF experiment side-effects may themselves effect climate and ecosystem changes that have unexpected negative outcomes (Fuhrman and Capone, 1991). Therefore, it is not surprising that the OIF validation and usefulness has been a subject of debate (Williamson et al., 2012).

OIF experiments have measured climate-relevant gases (*i.e.*, N₂O, CH₄, dimethylsulfide, and halogenated volatile organic compounds) that are produced by biological activity and/or photochemical reaction (Liss et al., 2005) to investigate change before and after iron addition. CH₄ has been considered to be relatively low risk as most of the CH₄ formed in the ocean is used as energy source for microorganisms and is converted to CO₂ before reaching to the sea surface (Smetacek and Naqvi, 2008; Williamson et al., 2012). Measurements of dissolved CH₄ during the SOFeX-N showed slightly elevated concentrations at less than 1 % (Wingenter et al., 2004). Simulated Southern Ocean large-scale iron fertilization has suggested that enhancement of CH₄ emission would offset only <1 % of the resulting carbon sequestration (Oschlies et al., 2010). On the other hand, the ocean is already a significant source for atmospheric N₂O, which has relatively the long lifetime (~110 years) in the atmosphere and has a global warming potential about 300 times greater than CO₂ (Forster et al., 2007). Therefore, so any enhancement of biological production that might enhance N₂O emission could work to increase atmospheric greenhouse gas levels rather than decrease them (Bange, 2006). During the SOIREE experiment, a significant increase (~7 %) in mean N₂O saturation in the pycnocline of the fertilized patch was associated with increased phytoplankton biomass. N₂O production was observed in the pycnocline after iron addition (Law and Ling, 2001). Measurements of N₂O saturation during SERIES also showed increases of 8 % at 30–50 m, which were coincident with the accumulation of ammonium and nitrite attributable to bacterial remineralization (Boyd et al., 2004; Law, 2008). Model estimates suggested that potential N₂O production on longer timescales (6 weeks) would subsequently offset by 6–12 % increased carbon reduction benefits resulting from remineralization of additional carbon fixed during SOIREE (Law and Ling, 2001). This estimate is in the same range as the N₂O offset of 6–18 % suggested by an earlier modeling study (Jin and Gruber, 2003) and the 5–9 % suggested by a more recent modeling study investigating the effectiveness of long-term and large-scale Southern Ocean OIF (Oschlies et al., 2010). This

phenomenon was also illustrated in a modeling study of long term and large scale OIF (Jin and Gruber, 2003). Complicating the story, however, excess N₂O was not found after iron addition during EIFEX, which showed significant vertical export with formation of rapidly sinking aggregate (Walter et al., 2005; Law, 2008). An explanation for the absence of N₂O accumulation below EIFEX patch might be limited bacterial remineralization by rapid export to the seafloor ~~the second longest experiment (-39 days)~~ (Walter et al., 2005).

Unlike N₂O emissions which have the potential to offset the effectiveness of OIF, Dimethylsulfide (DMS), hypothesized to be a precursor of sulfate aerosols that cause cloud formation and so climate cooling, may contribute to the homeostasis of the earth's climate by countering warming from increasing CO₂ (Charlson et al., 1987). The DMS response to iron addition was measured during all OIF experiments. In equatorial Pacific and Southern Ocean, DMS increased, but in the subarctic Pacific, it remained constant or decreased (Lawrence, 2002; Boyd et al., 2007). ~~was measured during all OIF experiments (Lawrence, 2002).~~ Significant short-term increases in DMS production were found in some of the OIF experiments (i.e., IronEx-2, SOIREE, EisenEx, and SOFeX-N) (Turner et al., 1996; Turner et al., 2004; Wingenter et al., 2004; Liss et al., 2005). The maximum DMS production observed was a ~~In particular, DMS production increased 6.5-fold increase~~ after iron addition during SOIREE (Turner et al., 2004). Similarly, a 5-fold enhancement of DMS was observed during SOFeX-N. Estimates derived by extrapolation of SOFeX-N DMS results to the Southern Ocean OIF experiment with 2 % areas suggested that iron fertilization would enhance DMS production by 20 %, which would lead to a 2 °C decrease in air temperature over the Southern Ocean (Wingenter et al., 2007). Interestingly, ~~However,~~ there were no significant changes in DMS production after iron addition during IronEx 1, in SEEDS-1, and SEEDS-2, despite increases in primary production (Turner et al., 1996; Takeda and Tsuda, 2005; Nagao et al., 2009). Contrast to SEEDS-1 and SEEDS-2, DMS production decreased in SERIES experiment ~~In the SERIES experiment, DMS production decreased due to the relatively high bacterial dimethylsulfoniopropionate (DMSP) metabolism (Levasseur et al., 2006), which is precursor of DMS production.~~ It is therefore clear that there are yet unknown factors affecting iron-induced DMS response, as it appears that OIF could be a significant source of DMS production in Southern Ocean and yet induce a DMS sink in subarctic Pacific. These results indicate that further observation-based and modeling studies are required to determine different features from place to place (Law, 2008).

~~Decomposition of iron addition enhanced biomass may cause decrease oxygen concentrations in the subsurface waters (Williamson et al., 2012). Box model solutions have further suggested that anoxic conditions may develop after OIF (Sarmiento and Orr, 1991). Although mid water oxygen depletion has not been reported during the OIF experiments to date, it has been suggested that OIF induced oxygen depletion may be occurred by increased downward carbon exports that elevate microbial respiration (Fuhrman and Capone, 1991).~~

~~Dimethylsulfide (DMS), hypothesized to be a precursor of sulfate aerosols that cause cloud formation and so climate cooling, was measured during all OIF experiments (Lawrence, 2002). Significant increases in DMS production were found in some of the OIF experiments (i.e., IronEx 2, SOIREE, EisenEx, and SOFeX N) (Turner et al., 1996; Turner et al., 2004; Wingenter et al., 2004; Liss et al., 2005). In particular, DMS production increased 6.5 fold after iron addition during SOIREE (Turner et al., 2004). However, there were no significant changes in DMS production after iron addition during IronEx 1, SEEDS 1, and SEEDS 2, despite increases in primary production (Turner et al., 1996; Takeda and Tsuda, 2005; Nagao et al., 2009). In the SERIES experiment, DMS production decreased due to the relatively high bacterial dimethylsulfoniopropionate (DMSP) metabolism (Levasseur et al., 2006), which is precursor of DMS production.~~

Halogenated volatile organic compounds (HVOCs, such as CH₃Cl, CH₃Br, and CH₃I), well known for their ability to

destroy ozone in the lower stratospheric ozone and marine boundary layer (Solomon et al., 1994), were also measured during the OIF experiments (Wingenter et al., 2004; Liss et al., 2005). During SOFeX-N experimentation, iron addition results for HVOC were complicated: CH₃Cl concentrations remained unchanged; CH₃Br concentrations increased by ~14 %; and while generally CH₃I concentrations decreased by ~23 % (Wingenter et al., 2004). CH₃I concentrations increased 2-fold in EisenEx (Liss et al., 2005). Therefore, as the DMS response above, further study is needed to understand the complexity of the HVOC response.

Decomposition of iron addition-enhanced biomass may cause decrease oxygen concentrations in the subsurface waters (Williamson et al., 2012). Although mid-water oxygen depletion has not been reported during the OIF experiments to date, it has been suggested that OIF-induced oxygen depletion may occur as increased downward carbon exports elevate microbial respiration (Fuhrman and Capone, 1991). Early studies using box model solutions have further suggested that anoxic conditions may develop after OIF (Sarmiento and Orr, 1991). However, more sophisticated and realistic models associated with OIF-induced oxygen changes in water columns showed well-oxygenated conditions without developing anoxic conditions (Oschlies et al., 2010; Keller et al., 2014). Box model solutions have further suggested that anoxic conditions may develop after OIF (Sarmiento and Orr, 1991). Although mid-water oxygen depletion has not been reported during the OIF experiments to date, it has been suggested that OIF-induced oxygen depletion may be occurred by increased downward carbon exports that elevate microbial respiration (Fuhrman and Capone, 1991).

The change of phytoplankton community composition after iron addition discussed in Section 2.4 may also have also ~~has~~ unintended consequences, in particular, toxin production (Silver et al., 2010; Trick et al., 2010). Some OIF experiments (including IronEx-2, SOIRE, EisenEx, and SOFeX-N/S) generated large blooms of diatoms dominated by pennate diatoms belonging to the genus ‘Pseudo-nitzschia’ (de Baar et al., 2005; Trick et al., 2010). Some species of the genus ‘Pseudo-nitzschia’ have the capacity to produce the neurotoxin domoic acid (DA) that is known to detrimentally affect marine ecosystems. For example, during IronEx-2 and SOFeX-S, high cell abundances of ‘Pseudo-nitzschia’ (106 and 105 cells l⁻¹, respectively) combined with moderate DA quotas (0.05 and 1 pg DA cell⁻¹, respectively) produced toxin levels as high as 45 ng DA l⁻¹ in IronEx-2 and 220 ng DA l⁻¹ in SOFeX-S; i.e., toxin levels that is able to cause certain damages to marine communities in coastal waters (Silver et al., 2010). In-situ measurements and ship-board culture experiments showed that iron enrichment stimulated growth of the toxigenic diatom genus ‘Pseudo-nitzschia’, known to produce neurotoxin domoic acid (DA) that has detrimental marine ecosystem impacts (Trick et al., 2010). For example, during IronEx 2 and SOFeX S, diatoms belonging to the genus ‘Pseudo-nitzschia’ dominated the phytoplankton community and high levels of DA were produced (45 ng of DA l⁻¹ in IronEx 2 and 220 ng of DA l⁻¹ in SOFeX S; Silver et al., 2010). However, no DA was found during EisenEx, even though diatom species of the genus generally ‘Pseudo-nitzschia’ were dominant numerically was the dominant diatom bloom species (Gervais et al., 2002; Assmy et al., 2007).

The direct and indirect environmental consequences of OIF remain unresolved due to inconsistent, highly uncertain outcomes (Williamson et al., 2012; Johnson and Karl, 2002; Chisholm et al., 2001), suggesting that we haven’t yet reached to ~~the a~~ conclusion of OIF experimentation as a carbon removal strategy (Boyd et al., 2007). Therefore, evaluation and prediction are paramount. It continues to be a valuable exercise to ~~attempt seek to~~ answers to scientific questions about the ~~efficiency~~ effectiveness of OIF as a means of reducing atmospheric CO₂ as well as to quantify ~~the~~ possible OIF side effects. In particular, potential trace gas emissions such as N₂O and DMS, which are influenced by the remineralization of sinking particles that follows OIF-induced blooms, are important to understand. They can directly and indirectly modify the desired carbon sequestration effectiveness and they can do so both positively and negatively. Therefore, monitoring of N₂O and DMS to

evaluate the effectiveness of OIF as a geoengineering approach is essential.

3.2 International law of the sea to OIF ~~Designing future OIF experiments: Direction and Considerations~~

To date, assessment of the effectiveness of OIF has been limited by the small area of the fertilized patches (25–300 km²) used in the experiments (Fig. 6a). Patch sizes have been limited in part due to the time and expense of comparing fertilized and unfertilized areas (ACE CRC, 2008). Nevertheless, as these small-scale OIF experiments have demonstrated considerable potential for easily and efficiently reducing atmospheric CO₂ levels, physical/biogeochemical/ecological models and natural (long-term) iron fertilization experiments have been studied in an effort to overcome some of the limitations of short-term iron-addition experiments and to predict the effectiveness of long-term and large-scale fertilization (Aumont and Bopp, 2006; Blain et al., 2007; Denman, 2008; Pollard et al., 2009). Earlier simplistic global biogeochemical models suggested that massive fertilization could draw down atmospheric CO₂ by as much as 107 ppm in 100 years (Joos et al., 1991; Peng and Broecker, 1991; Sarmiento and Orr, 1991; Kurz and Maier-Reimer, 1993). Recent global models with a more realistic ecosystem and biogeochemical cycles predict values closer to 33 ppm drawdown in atmospheric CO₂. These results suggest that the amount of carbon sequestration resulting from OIF would represent only a modest offset, a contribution less than 10 % for the range of IPCC future emissions scenarios (Aumont and Bopp, 2006; Denman, 2008). Natural OIF experiments also showed much higher carbon sequestration rates than the small-scale OIF experiments (Morris and Charette, 2013), suggesting that there may be scaling or timing issues in the smaller experiments that preclude simple scaling-up as a prediction tool (see discussion in Section 4). For this reason, several commercial companies (e.g., GreenSea Venture and Climos, <http://www.greenseaventure.com>; <http://www.climos.com>) have been promoting large-scale commercial OIF experiments as a climate mitigation strategy and a means to gain carbon credits (Chisholm et al., 2001; Buesseler and Boyd, 2003). However, this effort has not been able to move forward because we have little knowledge about the potential magnitude of possible side effects related to large-scale geoengineering OIF. It remains difficult to extrapolate findings from the small-scale OIF experiments because the environmental/ecosystem side effects from these miniature studies are themselves quite variable and not yet clearly understood. However, presently available studies do indicate that the known side effects from small-scale studies are themselves small-scale. It therefore seems reasonable that we should continue to undertake small-scale studies to better assess these risks and so lay the groundwork for evaluating the potential efficacy and impacts of large-scale OIF as a geoengineering solution to anthropogenic change.

With potential risks and benefits of OIF, there have been legal issues surrounding OIF raised to support the further study and increase understanding of OIF (Williamson et al., 2012). At present, large-scale and/or commercial OIF experiments are banned by international regulation. The international Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter (London Convention, 1972) and Protocol to the London Convention (London Protocol, 1996) placed legal restrictions on dumping of wastes and other matter that cause hazard, harm, and damage in the ocean and/or interfere with the marine environment. In 2007, the London Convention & Protocol (LC/LP) scientific groups released a statement of concern about ocean fertilization and recommended that ocean fertilization activities be evaluated carefully to ensure that such operations were not contrary to the aims of the LC/LP. Under the LC/LP, commercial activities are prohibited, and only ‘small-scale’ legitimate scientific research in ‘coastal waters’ is allowed (Resolution LC-LP.1 (2008), 2008). LC/LP also developed an assessment framework for scientific ocean fertilization research to be applied on a case-by-case basis founded on the agreed definition and compliance with the aims and objectives of Resolution LC-LP.1 (2008) (Fig. 9) (Assessment Framework for

Scientific Research Involving Ocean Fertilization, 2010). This framework demands preliminary scientific research to get a permission for OIF experimentation as transparent/reasonable scientific rationale/purpose and risk analysis undertaken using parameters such as problem formulation, site selection, exposure assessment, effects assessment, risk characterization, and risk management must be provided (Assessment Framework for Scientific Research Involving Ocean Fertilization, 2010).
5 Monitoring is also required an integral component of all approved (i.e., legitimate) scientific research activity to assess ecological impacts and to review actual versus intended geoengineering benefits (ACE CRC, 2015). In October 2013, LC/LP categorized artificial ocean fertilization as marine geoengineering, thereby prohibiting operational OIF activities, but enabling OIF scientific research that meets the permit conditions through the environmental assessment framework (Resolution LP.4 (8), 2013).

4 Future: Considerations for designing future OIF experiments

~~3.2 Designing future OIF experiments: Direction and Considerations~~

Scientific research on OIF has focused on improving our understanding of the ~~efficiency~~effectiveness, capacity, and risks of OIF as an atmospheric CO₂ removal strategy. Although the first OIF experiments took place more than twenty years
15 ago, the legal and economic aspects of such a strategy in terms of international laws of the sea and carbon offset markets are not yet clear (ACE CRC, 2015). It is therefore of paramount importance that future OIF experiments continue to focus on the ~~efficiency-effectiveness~~ and capacity of OIF as a means of reducing of atmospheric CO₂, but in doing so should carefully consider iron addition method (i.e., ‘How’), tracking methods and measurement parameters (i.e., ‘What’), locations (i.e., ‘Where’), timing (i.e., ‘When’), and duration (i.e., ‘How long’)~~major factors such as amount/patch size associated with iron addition (i.e., ‘How’), location (i.e., ‘Where’), and timing (i.e., ‘When’)~~ to build on the results of OIF experiments, ~~as to~~
20 develop our understanding of the magnitude and sources of uncertainties and in so doing build confidence in our ability to reproduce results.

How: The first consideration for a successful OIF experiment lies in the strategy/approach to maintain added iron within the upper mixed layer. During the first OIF experiment,- IronEx-1 is a good example of a successful OIF experiment. The
25 IronEx-1, the patch was fertilized with acidified iron(II) sulfate according to the target concentrations of 3.6 nM because iron-enrichment bottle incubation experiments performed in deck-board incubators using ocean water suggested maximum phytoplankton growth rates in response to iron additions of 1–2 nM (Fitzwater et al., 1996). However, subject to horizontal dispersion, concentrations of iron added in the open ocean rapidly decreased from 3.6 nM to 0.25 nM in just four days. Further, the magnitude of the open ocean biogeochemical response was less than bottle enrichment experiments suggested (Coale et al., 1998). Seeking to sustain enhanced iron concentrations in patches, since IronEx-2, the technique of applying repeated (2 to 4) iron infusions has been used in all OIF experiments except SEEDS-1 and FeeP (de Baar et al., 2005; Boyd et al., 2007). Like IronEx-1, SOIREE showed that losses in dissolved iron after the first iron infusion rapidly increased due to horizontal dispersion, and also noted loss due to oxidation of the additional iron(II) to iron(III) (Bowie et al., 2001). However, SOIREE demonstrated that four additions of iron with intervals of about 3 days led to a persistent elevation of both dissolved and
30 particulate iron within the mixed layer at the end of the experiment through fast reduction combined with an increase in the concentration of iron-binding ligands after multiple infusions. Both EIFEX and SOFeX-S also found that multiple iron(II) infusions allowed iron to persist in the mixed layer longer than its expected oxidation times. They determined that the relatively low oxidation rates were related to a combination of photochemical production, slow oxidation, and possibly organic complexation (Croot et al., 2008). Blain et al. (2007) explained that the higher carbon sequestration effectiveness of natural
35 OIF experiments compared to artificial OIF experiments partly resulted from the slow and continuous iron addition that occurs
40

in the natural environment. Short-term infusions of large amounts of iron tend to lead the substantial loss of artificially added iron. Therefore, to increase ration of the amount of carbon flux exported to the amount of iron supplied, multiple additions of iron are more efficient.

What: The second consideration for a successful OIF experiment is effective tracing of fertilized patch including detection of carbon sequestration (Buesseler and Boyd, 2003) and monitoring of possible side effects. OIF side effects include emission of climate-relevant gases such as N_2O and DMS that directly contribute to warming and cooling of the environment, respectively (Law, 2008). During IronEx-1, the fertilized patch was subsequently traced with large variety of physical-biogeochemical techniques and parameters such as GPS and ARGO equipped drifting buoys, SF_6 , Fv/Fm ratio, pCO_2 , and chlorophyll fluorescence using underway sampling systems, and satellite images (Martin et al., 1994; Coale et al., 1998). As IronEx-1 provided potential evidence to support Martin's iron hypothesis by showing an increase in phytoplankton bloom with iron enrichment, many subsequent OIF experiments adopted the tracing methods introduced by IronEx-1, and were similarly able to detect environmental changes through the observation of both physical and biogeochemical parameters before and after iron addition (Martin et al., 1994; Coale et al., 1996; Boyd et al., 2000; Tsuda et al., 2005; Coale et al., 2004; Boyd et al., 2004; Smetacek et al., 2012). Carbon export fluxes can be detected using ^{234}Th , $^{13}C_{org}$, free-drifting sediment traps, beam-transmissometers, and UVPs (Table 5) (Bidigare et al., 1999; Nodder et al., 2001; Boyd et al., 2004; Buesseler et al., 2004; Coale et al., 2004; Aono et al., 2005; Tsuda et al., 2007; Smetacek et al., 2012; Martin et al., 2013). In particular, it is possible to evaluate the temporal evolution of iron-induced export carbon fluxes into deeper waters by applying the thorium deficiency method and sediment trap fluxes that were used during previous OIF experiments (Table 5). Because of their high vertical resolution, the profiling transmissometer, the UVP with its camera that photographs particles, and transmissometers riding on profiling autonomous floats could provide a record of temporal evolution in POC stocks through successive depth layers once calibrated using POC measurements (Smetacek et al., 2012; Martin et al., 2013). Future OIF experiments could benefit from these technological advances so as to more efficiently trace carbon export flux at higher vertical and temporal resolution than has been done in the past. Nevertheless, the application of multiple methods including trap fluxes and ^{234}Th deficiency to provide relatively direct flux estimates combined with autonomous profilers with their higher resolution would produce the best results and was subsequently traced with large variety of physical-biogeochemical techniques and parameters such as GPS and ARGO equipped drifting buoys, SF_6 , Fv/Fm ratio, pCO_2 , and chlorophyll fluorescence using underway sampling systems (Martin et al., 1994). Many subsequent OIF experiments adopted the methods introduced from the IronEx-1, and were similarly able to detect environmental changes through the observation of both physical and biogeochemical parameters before and after iron addition (Martin et al., 1994; Coale et al., 1996; Boyd et al., 2000; Tsuda et al., 2005; Coale et al., 2004; Boyd et al., 2004; Smetacek et al., 2012). This success suggests that there is no need to completely redesign OIF experimentation as the previous designs and methods are a good reference for future efforts.

Where: The ~~third~~ ~~second~~ consideration for a successful OIF experiment is the ~~selection of~~ location selection. The dominance of diatoms in phytoplankton communities plays major role in biological pump efficiency because some species of diatom rapidly sink in aggregate formations and have high accumulation rates of heavily silicified frustules (Tréguer et al., 1995). On the other hand, mesozooplankton (i.e., copepods) graze on large diatoms and so are a major limiting factor in diatom production (Coale et al., 2004; Tsuda et al., 2007). Therefore, to obtain the greatest possible carbon export flux in response to iron addition, OIF experiments should be designed in regions with high silicate concentrations and low copepod abundances. In selecting sites for iron fertilization, ~~To easily and efficiently observe iron-induced changes,~~ it is also important to isolate the iron-fertilized patch from the surrounding unfertilized waters ~~to easily and efficiently observe iron-induced changes~~ (Coale et al., 1996). Ocean eddies provide an excellent setting for OIF experimentation as they have physically rotating water column structures, that naturally tend to isolate interior waters from the surrounding waters. Mesoscale eddies range from 25–250 km

in diameter and maintain their characteristics for 10–100 days after formation (Morrow and Traon, 2012). Eddy centers, in which fertilization is performed, tend to be subject to relatively slow current speeds compared to the surrounding environment and have high vertical coherence, providing ideal conditions for tracing the same water column from the surface to the deep during the experiment with the vertical coherence (Smetacek and Naqvi, 2008). Iron additions were carried out at the center of eddies in EisenEx, EIFEX, and LOHAFEX conducted in the Southern Ocean (Smetacek, 2001; Smetacek and Naqvi, 2008; Smetacek and Naqvi, 2010; Smetacek et al., 2012). Observations were also made outside the eddy core well away from the iron-fertilized patch to provide similar information about environmental conditions to compare with patch observations. EIFEX showed a clear difference in export carbon flux between waters within the patch and external to the patch (Smetacek et al., 2012). Therefore, finding of an appropriate eddy setting in a study area should be one of the high priority considerations in conducting an OIF experiment (Smetacek and Naqvi, 2008).

When: The ~~fourth third~~ consideration for successful OIF experiment is timing including when an experiment starts, which can be broken down into when an experiment starts and how long it lasts. Primary production in ocean environment is generally limited by nutrient availability and/or by light availability, often referred to as single- or co-limitation. Primary production in the Southern Ocean, a representative HNLC region, is subject to co-limitation by micro-nutrients (i.e., iron) and light availability (Mitchell et al., 1991). Previous Southern Ocean OIF experiments have been conducted from spring to late summer, and revealed that during this time of year primary production is limited by iron supply rather than light availability (de Baar et al., 2005; Smetacek and Naqvi, 2008; Peloquin et al., 2011). However, the most opportune time, to distinguish phytoplankton blooms increased by iron addition from natural blooms, is during the month of March when natural phytoplankton blooms decline in the Southern Ocean.

How long: The fifth consideration for successful OIF experiment is how long it lasts. Duration: Although it has been reported that the periods that phytoplankton blooms have been maintained by OIF have lasted from ~10 to 40 days (Martin et al., 1994; Coale et al., 1996; Boyd et al., 2000; Tsuda et al., 2005; Coale et al., 2004; Boyd et al., 2004; Smetacek et al., 2012), it has also been suggested that most OIF experiments did not cover the full response times from onset to termination (Boyd et al., 2005). For example, SOIREE and SEEDS-1, had relatively short observation periods (~13 days) and saw increasing trends in primary production throughout the experiments (Fig. ~~9a~~10a) suggesting that the observation period should have been extended. Furthermore, after the end of SOIREE, ocean color satellite images showed continued high chlorophyll-a concentrations (~1 mg m⁻³) in the iron fertilized patch, which was seen as a long ribbon shape that extended some ~150 km for ~46 days; (~7 weeks) after the initial iron addition (Fig. ~~9b~~10b) (Abraham et al., 2000). This result indicates that short experiment periods may not be sufficient for detecting the full influence of artificial iron addition on primary production (Fig. 8b) (Boyd et al., 2000; Tsuda et al., 2003; de Baar et al., 2005). However, SERIES, SEEDS-2, EIFEX, and LOHAFEX did ~~Among OIF experiments, EIFEX, the second longest at ~39 days, fully monitored~~ all the phases of the phytoplankton bloom from onset to termination. Among OIF experiments, EIFEX, the second-longest at ~39 days, and it alone observed iron-induced deep export production between 30 and 36 days after iron addition (Fig. 8a and ~~9a~~10a) (Assmy et al., 2013; Smetacek et al., 2012). Furthermore, long-term observation period covering the later stage of bloom development during natural OIF experiments has made it possible to obtain high carbon sequestration effectiveness (Blain et al., 2007; Pollard et al., 2009). It is therefore important to predict both the needed time for onset and the time required for the response to run its full course, otherwise it ~~is not possible to~~will not be possible to quantify the net effect. In addition, to detect the enhancement of the carbon export flux to iron addition, the observation period should last at least 35 to 40 days after iron addition.

In conclusion, to maximize the effectiveness of OIF experiments in the future, we suggest a design that incorporates: ('How') multiple iron additions to 1–2 nM concentration; ('What') multiple means of tracing the fertilized patch including

both trap fluxes and/or ^{234}Th deficiency to obtain direct flux estimates and autonomous platforms such as gliders, equipped with biogeochemical sensors, to obtain high vertical resolution, and monitoring side effect such as N_2O and DMS; ('Where') in an eddy structure with high silicate concentration and low copepod abundance; ('When') e.g., March in the Southern Ocean; ('How long') at least $>\sim 35$ days.

To date, assessment of the effectiveness of OIF has been limited by the small area of the fertilized patches (25–300 km^2) used in the experiments (Fig. 6a). Patch sizes have been limited in part due to the time and expense of comparing fertilized and unfertilized areas (ACE, 2008). However, since these small scale OIF experiments have demonstrated considerable potential for easily and efficiently reducing atmospheric CO_2 levels, several commercial companies (e.g., GreenSea Venture and Climos, <http://www.greenseaventure.com>; <http://www.elimos.com>) have been promoting large scale commercial OIF experiments as a climate mitigation strategy and a means to gain carbon credits (Chisholm et al., 2001; Buesseler and Boyd, 2003). However, this effort has not been able to move forward because the large uncertainties remaining in the technique mean that potential risks to the environment/ecosystem by even small scale OIF experiments are not yet well understood. At present, large scale and/or commercial OIF experiments are banned by international regulation (Williamson et al., 2012). The international Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter (London Convention, 1972) and Protocol to the London Convention (London Protocol, 1996) placed legal restrictions on dumping of wastes and other matter that cause hazard, harm, and damage in the ocean and/or interfere with the marine environment. In 2007, the London Convention & Protocol (LC/LP) scientific groups released a statement of concern about ocean fertilization and recommended that ocean fertilization activities be evaluated carefully to ensure that such operations were not contrary to the aims of the LC/LP. Under the LC/LP, commercial activities are prohibited, and only "small scale" legitimate scientific research in "coastal waters" is allowed (Resolution LC-LP.1 (2008), 2008). LC/LP also developed an assessment framework for scientific ocean fertilization research to be applied on a case-by-case basis founded on the agreed definition and compliance with the aims and objectives of Resolution LC-LP.1 (2008) (Fig. 10) (Assessment Framework for Scientific Research Involving Ocean Fertilization, 2010). This framework demands preliminary scientific research to get a permission for OIF experimentation as transparent/reasonable scientific rationale/purpose and risk analysis undertaken using parameters such as problem formulation, site selection, exposure assessment, effects assessment, risk characterization, and risk management must be provided (Assessment Framework for Scientific Research Involving Ocean Fertilization, 2010). Monitoring is also required an integral component of all approved (i.e., legitimate) scientific research activity to assess ecological impacts and to review actual versus intended geoengineering benefits (ACE, 2015). In October 2013, LC/LP categorized artificial ocean fertilization as marine geoengineering, thereby prohibiting operational OIF activities, but enabling OIF scientific research that meets the permit conditions through the environmental assessment framework (Resolution LP.4 (8), 2013).

5. Design for a Korean Iron Fertilization Experiment in the Southern Ocean (KIFES)

5.1 Background - Bransfield Basin

4. Future: Introduction to the Korean Iron Fertilization Experiment in the Southern Ocean (KIFES) project

4.1 Background for KIFES

The last artificial OIF experiment, LOHAFEX was led by scientists from CSIR-National Institute of Oceanography in Goa, Alfred-Wegener Institute for Polar and Marine Research (AWI) in Bremerhaven, and 5 other nations. The German government suddenly halted LOHAFEX just before the departure of RV *Polarstern* from the port following protests by NGOs

and environmentalists against OIF experimentation due to concern about direct and long-term side effects of artificial iron fertilization on marine ecosystem. To ~~datadate~~, the only OIF experiment with ~~a~~-scientific and legal review processes was 'LOHAFEX' conducted in the Southern Ocean. Although people are still worried about side effects of OIF and scientists are still curious about the measurable effects of OIF on the ocean environment, there have been no further intensive investigations to fill the gap between supporters and opponents of OIF as ~~the a~~ geoengineering approach since LOHAFEX. There are still many unknowns to be investigated about OIF experiments.

The paleoclimate team at Korea Polar Research Institute (KOPRI) found ~~the~~ geological evidence of intensive organic carbon burial in the sediments (Yoo et al., 2016), which removes atmospheric CO₂, in the eastern Bransfield Basin on the Antarctic Peninsula. The diatomaceous ooze layer was well preserved in the buried sediments of the Bransfield Basin (Bahk et al., 2003; Kang et al., 2003; Bak et al., 2015), and represents the fast sinking of diatoms within a short time. Scientists at KOPRI suspect that enhancement of the diatom flux ~~might may~~ be related to input of bioavailable iron that controls phytoplankton population by allowing efficient use of surface nutrients in the Southern Ocean. In addition, ~~this oceanographic (physical biogeochemical geological) parameters might be ascribed to the~~ unique increase ~~of in~~ diatom production, the fast sinking rate of the organic matters, and the remarkably well-preserved well preservation of organic carbon sediments in this area, suggest the existence of a strong 'biological pump (i.e., significant export production)'. This type of 'bottom-up' approach (see potential for a surface source by looking at the sedimentary evidence) has not been considered in the location selection for previous experiments. Therefore, it is expected that OIF in diatom-dominated eastern Bransfield Basin will be effective for carbon export. ~~However, the exact driving force for this unique process should be intensively investigated prior to the OIF experiment.~~

~~Timely, a~~ science-oriented iron fertilization project, KIFES (Fig. 11), was launched ~~by the Korean oceanographers~~ in 2016 with the research funding supported by the Korean Ministry of Oceans and Fisheries. This project ~~was planned will be led~~ mainly by KOPRI with domestic collaborators (i.e., Incheon National University, Inha University, Pusan National University, Hanyang University, and Yeonsei University) and strengthened by international collaborators (i.e., AWI, Institute of Geological and Nuclear Sciences, MIT-WHOI, University of Otago, University of California at Irvine, McMaster University, University of South Florida, Royal Netherlands Institute for Sea Research, and Dalhousie University). The main purpose of ~~the KIFES project was~~ (1) to evaluate the effectiveness of artificial OIF in terms of atmospheric carbon sequestration (i.e., effectiveness in export production) in the Southern Ocean, (2) to determine the environmental conditions that would maximize effectiveness of artificial OIF, and (3) to reveal short- and long-term side effects derived from a small-scale artificial OIF experiment. Unfortunately, KIFES has lost its present funding source. Nevertheless, optimism prevails that alternative funding will be found at a future date and the following section (5.2) is intended to provide a basic set of design guidelines with expectation that an opportunity to move forward with KIFES will occur in near future. ~~is (1) to further understand the role of iron for atmospheric carbon sequestration in the Southern Ocean, (2) to verify proper environmental conditions to maximize effectiveness of OIF experiment, and (3) to reveal short and long term side effects derived from artificial OIF experiment.~~

5.2 A plan for the future: KIFES

4.2 KIFES Plans

The KIFES design entails a 5-year project plan. It would model the 'EIFEX' program that found deep carbon by conducting an OIF experiment in an eddy structure. The KIFES project would include a preliminary environmental survey in

the eastern Bransfield Basin, a preliminary environmental survey both outside and inside an eddy structure, an OIF experiment, and an assessment of the full KIFES project. In this section, we introduce the major goal, objective, and main tasks of KIFES.

The KIFES project is 5 year plan project (2016–2020). This project includes two preliminary environmental surveys, a preliminary OIF test, the KIFES OIF experiment, and an assessment of the KIFES project. In this section, we introduce the major goals and main tasks of KIFES project.

4.5.2.1 Year one plan First project year (2016 underway)

Goals: To gather information about oceanographic conditions in the eastern Bransfield Basin (eBB) including both eddy development and distribution.

Objective: To understand as best we can the physical and biogeochemical oceanography if relevance to the eBB through analysis of earlier data sets and review of published papers. Determination of KIFES OIF experiment sites and establishment of an international OIF network

Main tasks: (1) Database of physical and biogeochemical parameters from previous surveys conducted in the eastern Bransfield Basin; (2) Review of eBB oceanographic conditions using data analysis and references; (3) Design of oceanographic cruise map for the first preliminary eBB survey, based on results from tasks (1) and (2); (4) Analysis of eddy development and distribution using satellite data in the eBB; (1) Investigation of earlier OIF locations and experiments to produce a database of physical and biogeochemical parameters from *in situ* observations and remote sensing data to select appropriate sites and to determine timing for an new OIF experiment in the eastern Bransfield Strait, (25) Preparation of scientific instruments for ocean physical and biogeochemical monitoring; (36) Establishment of an international collaborative OIF network; and (47) KIFES field program proposal preparation for approval of LC/LP.

4.5.2.2 Year two plan Second project year (2017)

Goal: First preliminary hydrographic survey to provide a foundational understanding of eBB oceanographic ocean environmental conditions.

Objective: (1) To gain information about oceanographic conditions from in-situ measurements in the eBB; and (2) To provide background information before KIFES experiment. in the eastern Bransfield Strait

Main tasks: (1) Using ice breaker RV *ARAON*, field investigation in the eBB of physical and biogeochemical parameters associated with both carbon sequestration as well as OIF side effect (e.g., N_2O), based on the first year task results; and, including side effect parameters such as N_2O in the eastern Bransfield Strait parameters and sites based on the 2016 investigation, and (2) Continued preparation of LC/LP proposal.

54.2.3 Year three plan Third project year (2018)

Goals: Preliminary hydrographic survey outside/inside eddy structure prior to the KIFES experiment.

Objective: To compare oceanographic conditions outside and inside an eBB eddy structure prior to the KIFES experiment. Second preliminary survey and a preliminary test of OIF in eddy structure prior to KIFES

Main tasks: (1) Detection of an eBB eddy using observations from acoustic Doppler current profilers and satellites; in

~~the eastern Bransfield Strait~~, (2) Intensive physical and biogeochemical field investigation both inside and outside an eddy structure; in the eddy, (3) Assessment of physical and biogeochemical properties outside vs. inside an eddy structure prior to KIFES experiment; Rehearsal of OIF experiment in the eddy structure, and (4) Submission of the LC/LP proposal to obtain approval for the KIFES experiment from International Maritime Organization.

5 54.2.4 Year four plan~~Fourth-year project (2019)~~

Goal: KIFES – OIF experiment in an eddy structure (Fig. 11).

Objective: To conduct the eBB artificial OIF experiment.

10 Main tasks: (1) Execution of the ~~The conducting of~~ KIFES field campaign, a scientific OIF experiment that will survey the region both inside and outside in an eddy structure in the ~~eBB eastern Bransfield Strait~~ employing underway sampling systems (e.g., such as high frequent $p\text{CO}_2$ and Oxygen/Argon ratios), gliders equipped with biogeochemical sensors, sediment traps deployed at multiple depths, sub-bottom profilers, and satellite observations; ~~multiple sediment traps, sub-bottom profilers, sediment coring systems, and satellite observations~~, and (2) Assessment ~~for~~ KIFES carbon sequestration effectsiveness and environmental (ocean and atmosphere) side effects

54.2.5 Year five plan ~~Fifth-year project (2020)~~

15 Goal: Integrated assessment of the KIFES project

Objective: To evaluate whether small-scale OIF experimentation can be an effective tool for detecting the effectiveness of artificially induced export production.

20 Main tasks: (1) Submission of the ~~KIFES OIF~~-assessment report; (2) Writing and sSubmission of scientific results to international journals; (3) Collection of feedback about the KIFES project from international scientific/oceanographic communities; and (4) Production of a final artificial OIF experiment summary (including Main tasks 1–3).

~~Preparation of the second stage of the KIFES project.~~

45.3 Expected results of KIFES~~Final Remark~~

25 None of the KIFES scientists has any interest in selling carbon credits by conducting OIF experiments. Rather, KIFES interest lies in the detailed investigation of the biogeochemical effects of artificial iron addition in the Southern Ocean and in the OIF evaluation as one possible geo-engineering method that might be used to mitigate the realities of the climate change effects we face. We look to a future where the KIFES project or one like it becomes a reality so that we may work towards providing a clear answer as to whether or not OIF is promising as a geo-engineering solution. The KIFES project would provide fundamental information and guidelines for future OIF experiments in HNLC regions. In particular, the aforementioned risks and side effects of OIF will be thoroughly investigated so as to belay international concern. And lastly, we emphasize that international cooperation is essential for a project as organizationally and scientifically complex as KIFES, which seeks to improve of our outlook for the Earth's future. KIFES will be performed after a decade long gap since LOHAFEX. None of the KIFES scientists have any interest in selling carbon credits by conducting OIF experiments. Rather, our interest lies in the detailed investigation of the biogeochemical effects of iron addition in the Southern Ocean and in the OIF evaluation as one

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of possible geo-engineering methods that might be used to mitigate the realities of the climate change effects we face. We hope that the 5 year KIFES project can give a clear answer as to whether or not OIF is a promising as a geo-engineering solution. The KIFES project will provide fundamental information and guidelines for future OIF experiments in HNLC regions. In particular, the aforementioned risks and side effects of OIF will be thoroughly investigated so as to belay international concern. Likewise, international cooperation is essential for the successful performance of KIFES and for improvement of our outlook for the Earth's future.

6.5 Summary

To test the Martin's hypothesis, a total 13 artificial OIF experiments for scientific study were conducted in the HNLC regions during the last 25 years. The biogeochemical responses to OIF experiments were observed in the increases of primary production as a result of drawdowns of macro-nutrients and DIC. In most experiments, dominance of phytoplankton group tended to be shifted from small-sized groups to large-sized groups, resulting in diatom-dominated phytoplankton community. However, the effectiveness in export production enhancing ocean biological pump was not clearly confirmed by the OIF experiments, except in one, EIFEX. Likewise, the possible environmental side effects in response to iron addition, such as production of greenhouse gases, development of hypoxia/anoxia in water column, and toxic algal blooms, were not fully evaluated due to inconsistent outcomes with large uncertainty depending on OIF experiment conditions and settings. ~~Therefore, validation and suitability of artificial OIF for mitigation of increasing atmospheric carbon levels has been debated. To fully understand the efficiency, capacity, and risks of OIF, scientifically based and site limited OIF experimentation is needed to consider such major factors as amount/patch size associated with iron addition, location, and experiment length, including compliance with international OIF regulations. A timely 5 year iron fertilization project, KIFES was launched in 2016 under the leadership of KOPRI with the support of domestic/international collaborative networks. This project focuses on investigating the details of the biogeochemical responses to artificial iron addition in the Southern Ocean and assessing suitability of OIF as one possible carbon removal strategy under international maritime laws. Previously raised issues associated with the risks of OIF will be investigated during the KIFES project. In particular, monitoring of N₂O and DMS must be considered in determining effectiveness of OIF as a geoengineering approach because these potential trace gas emissions can directly and indirectly modify carbon reduction benefits resulting from OIF. Therefore, validation and suitability of artificial OIF for mitigation of rapidly increasing atmospheric CO₂ levels have been debated for three decades. At present, large-scale or commercial OIF experiments are prohibited by international regulation, so small-scale OIF experimentation with scientific purpose is permitted to understand the effectiveness, capacity, and risks of artificial OIF. To maximize effectiveness of OIF, future OIF experiments should be conducted by carefully considering the major factors such as the methods for iron addition, tracking methods, measurement parameters, location, timing, and experiment duration, under international OIF regulations. Finally, we look to a future the KIFES project or one like it becomes a reality so that we may work towards providing a clear answer as to whether or not OIF is promising as a geo-engineering solution.~~

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Table 1. Summary of OIF experiments; time, location, research vessel, amounts of Fe addition (day of Fe addition from the beginning of OIF experiment), background Fe concentrations, Fe concentrations after Fe additions, tracer, patch size fertilized by first Fe addition, experiments periods, and characteristics of study regions.

	Experiment	Time	Location	Research Vessel	Fe (kg) (day)	Initial Fe (nM)	After Fe (nM)	Tracer	Patch size (km ²)	Period (days)	Region
1	IronEx-1	Oct 1993	5° S, 90° W Equatorial Pacific	RV <i>Columbus Iselin</i>	①450 (0)	0.06	3.60	SF ₆	64	10	HNLC
2	IronEx-2	May 1995	3.5° S, 104° W Equatorial Pacific	RV <i>Melville</i>	①225 (0) ②112 (3) ③112 (7)	0.02	2.00 1.00 1.00	SF ₆	72	17	HNLC
3	SOIREE	Feb 1999	61° S 141° E Southern Ocean- Australasian-Pacific sector	RV <i>Astrolab</i>	①768 (0) ②312 (3) ③312 (5) ④353 (7)	0.08	3.80 2.60 2.60 2.50	SF ₆	50	13	HNLC
4	EisenEx	Nov 2000	48° S, 21° E Southern Ocean- Atlantic sector	RV <i>Polarstern</i>	①780 (0) ②780 (7) ③780 (16)	0.06	2.00	SF ₆	50	23	HNLC
5	SEEDS-1	Jul–Aug 2001	48.5° N, 165° E North Pacific- Western subarctic gyre	RV <i>Kaiyo-Maru</i>	①350 (0)	0.05	2.90	SF ₆	80	13	HNLC
6	SOFEX-N	Jan–Feb 2002	56.23° S, 172° W Southern Ocean- Atlantic sector	RV <i>Revelle</i> RV <i>Melville</i>	①631 (0) ②631 (5) ③450 (30)		1.20	SF ₆	225	40	HNLC
7	SOFEX-S	Jan–Feb 2002	66.45° S, 171.8° W Southern Ocean- Atlantic sector	RV <i>Revelle</i> RV <i>Melville</i> RV <i>Polar star</i>	①315 (0) ②315 (4) ③315 (7) ④315 (11)		0.70	SF ₆	225	28	HNLC
8	SERIES	Jul-Aug 2002	50.14° N, 144.75° W North Pacific- Eastern subarctic Pacific	RV <i>John P. Tully</i> RV <i>El Puma</i> RV <i>Kaiyo Maru</i>	①315 (0) ②315 (6)	<0.10	2.00 0.60	SF ₆	77	25	HNLC

To be continued

	Experiment	Time	Location	Research Vessel	Fe (kg) (day)	Initial Fe (nM)	After Fe (nM)	Tracer	Patch size (km ²)	Period (days)	Region
9	EIFEX	Feb–Mar 2004	50° S, 2° E Southern Ocean-Atlantic sector	RV <i>Polarstern</i>	①1406 (0) ②1406 (13)	0.20	1.50 0.34		167	39	HNLC
10	FeeP	Apr–May 2004	27.5° N 22.5° W North Atlantic-Subtropical north-east Atlantic	RV <i>Charles Darwin</i> RV <i>Poseidon</i>	①1840 (0)	0.20	3.00	SF ₆	25	21	LNLC
11	SAGE	Mar–Apr 2004	46.7° S 172.5° E Southern Ocean-Southeast of New Zealand	RV <i>Tangaroa</i>	①265 (0) ②265 (6) ③265 (9) ④265 (12)	0.09	3.03 1.59 0.55 1.01	SF ₆	36	15	HNLCLSi
12	SEEDS-2	Jul–Aug 2004	48° N, 166° E North Pacific-Western subarctic gyre	RV <i>Hakuho-Maru</i> RV <i>Kilo-Moana</i>	①332 (0) ②159 (6)	0.17	1.38	SF ₆	64	26	HNLC
13	LOHAFEX	Jan–Mar 2009	48° S, 15° W Southern Ocean-Atlantic sector	RV <i>Polarstern</i>	①2000 (0) ②2000 (21)		2.00	SF ₆	300	40	HNLCLSi
1	CROZEX*	Nov 2004–Jan 2005	44° S, 50° E Southern Ocean-South of sub-Antarctic Front	RV <i>Discovery</i>		0.04	0.55				HNLC
2	KEOPS*	Jan–Feb 2005	50° S, 73° E Southern Ocean-South of Polar Front	RV <i>Marion Dufresne</i>							HNLC

* Natural OIF experiments

Sources are as follows: Martin et al., 1994; Coale et al., 1996; Coale et al., 1998; Boyd et al., 2000; Gervais et al., 2002; Tsuda et al., 2003; Boyd et al., 2004; Bakker et al., 2005; Boyd et al., 2005; Coale et al., 2004; de Baar et al., 2005; Hiscock and Millero, 2005; Nishioka et al., 2005; Tsuda et al., 2005; Tsumune et al., 2005; Boyd et al., 2007; Rees et al., 2007; Tsuda et al., 2007; Harvey et al., 2010; Law et al., 2011; Smetacek et al., 2012; Martin et al., 2013.

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Table 2. Summary of OIF experiments: objective, significant results, and limitation

	Experiment	Objective	Significant results	Limitation
1	IronEx-1	* To test the iron hypothesis	* Increased phytoplankton production in response to added iron	* Relatively small increase in primary production
2	IronEx-2	* To test four hypotheses which were raised by lack of biogeochemical response upon iron addition during IronEx-1	* A massive phytoplankton bloom response to iron addition * Significant drawdown of $p\text{CO}_2$ * Diatom-dominated community	* Rapid loss of iron within mixed layer * Limited information on export flux * No observation of the fate of the bloom
3	SOIREE	* To confirm of iron limitation in phytoplankton growth in the Southern Ocean * To understand downward fluxes	* Iron-induced decreases in $p\text{CO}_2$ * Diatom-dominated bloom with low mesozooplankton grazing	* No increase in export flux * Unknown remineralization
4	EisenEx	* To artificially stimulate an airborne 'dust' episode in the Southern Ocean with OIF * To study the response of phytoplankton bloom under limited light condition * To test the iron hypothesis in the subarctic North Pacific Ocean	* Maintenance of iron-induced phytoplankton bloom in austral spring	* No difference in POC flux between inside patch and outside patch in the eddy
5	SEEDS-1	* To examine the changes in the species composition and the specific growth responses of key diatom species	* Significant drawdown in $p\text{CO}_2$ * Shifting from oceanic diatoms to neritic centric diatom	* No increase in export flux * Unknown trophic interactions
6	SOFeX-N	* To investigate the effects of iron enrichment in regions with low silicate concentrations	* Enhanced growth of diatom groups * $p\text{CO}_2$ depressed by increased primary production	* Entrainment of dissolved silicate into the patch by physical mixing
7	SOFeX-S	* To investigate the effects of iron enrichment in regions with high silicate concentrations	* Increased POC flux out of the mixed layer	* Small POC flux relative to natural blooms
8	SERIES	* To detect the decline and fate of an iron-fertilized diatom bloom * To measure the response of trophic interactions to iron addition * To measure carbon flux out of the surface layer	* Decline and fate of iron-added bloom * Bacterial remineralization and mesozooplankton grazing accounting as main process of POC decrease	* Inefficient transfer of iron-increased POC below the permanent thermocline

To be continued

	<u>Experiment</u>	<u>Objective</u>	<u>Significant results</u>	<u>Limitation</u>
9	<u>EIFEX</u>	<u>* To find out the growth and demise phase of phytoplankton bloom in fertilized patch</u> <u>* To confirm the second condition of the iron hypothesis</u> <u>* To understand phosphate and iron limitation in biological activity</u>	<u>* Significant enhancement of deep carbon export (>3000 m)</u> <u>* The occurrence of rapidly sinking large aggregate</u> <u>* Increased <i>Trichodesmium</i></u>	<u>* No overall shift in phytoplankton community</u>
10	<u>FeeP</u>			
11	<u>SAGE</u>	<u>* To understand gas transfer processes and influence of OIF on biologically driven gas exchange</u>	<u>* Successful measurement of gas exchange at strong wind speeds</u>	<u>* No phytoplankton bloom</u> <u>* Increase in $p\text{CO}_2$ due to physical mixing</u>
12	<u>SEEDS-2</u>	<u>* To determine the fate of an iron-stimulated diatom bloom</u> <u>* To verify the vertical export carbon flux</u>	<u>* Higher abundance of mesozooplankton (copepod) during bloom-development phase</u>	<u>* No extensive diatom bloom</u>
13	<u>LOHAFEX</u>	<u>* To investigate the fate of iron fertilized bloom biomass related to heterotrophs and export flux under silicate-limiting conditions</u>	<u>* Recycled carbon by grazing and microbial food web in low silicate waters</u>	<u>* Lack of fertilization-induced export due to silicon limitation and bacterial remineralization</u>

Sources are as follows: Martin et al., 1994; Coale et al., 1996; Coale et al., 1998; Bidigare et al., 1999; Boyd et al., 2000; Charette and Buesseler, 2000; Gervais et al., 2002; Tsuda et al., 2003; Boyd et al., 2004; Coale et al., 2004; Bakker et al., 2005; Boyd et al., 2005; de Baar et al., 2005; Hiscock and Millero, 2005; Nishioka et al., 2005; Tsuda et al., 2005; Tsumune et al., 2005; Boyd et al., 2007; Rees et al., 2007; Tsuda et al., 2007; Harvey et al., 2010; Law et al., 2011; Smetacek et al., 2012; Martin et al., 2013

Table 3. Changes of chemical parameters from initial to after concentrations by OIF experiments. Note that *Δ[X] represents changes in concentrations (i.e., [X]_{post-fertilization} – [X]_{pre-fertilization}).

	Experiment	Initial NO ₃ (μM)	*ΔNO ₃ (μM)	Initial PO ₄ (μM)	*ΔPO ₄ (μM)	Initial Si (μM)	*ΔSi (μM)	Initial pCO ₂ (ppm)	*ΔpCO ₂ (ppm)	Initial DIC (μM)	*ΔDIC (μM)
1	IronEx-1	10.8	-0.70	0.92	-0.02	3.90	-0.02	471	-13.0	2044	-6.00
2	IronEx-2	10.4	-4.00	0.80	-0.25	5.10	-4.00	538	-73.0	2051	-27.0
3	SOIREE	25.0	-3.00	1.50	-0.24	10.0	-3.00	350	-(38.0– 32.0)		-(18.0– 15.0)
4	EisenEx	22.0	-1.00	1.60	-0.10	10.0	0	360	-(20–18)		-(15.0– 12.0)
5	SEEDS-1	18.5	-15.8			31.8	-26.8	390	-130		-58.0
6	SOFeX-N	21.9	-1.40	1.40	-0.09	2.50	-1.10	367	-26	2109	-14.0
7	SOFeX-S	26.3	-3.50	1.87	-0.21	62.8	-4.00	365	-36	2176	-21.0
8	SERIES	10.0– 12.0	-(9.00– 7.00)	>1.00	-0.50	14.0– 16.0	-(14.0– 12.0)	350	-85	2030	-37.0
9	EIFEX	25.0	-1.50	1.80	-0.30	19.0	-11.0	360	-30	2135	-13.5
10	FeeP	<0.01		0.01							<-1.00
11	SAGE	7.90– 10.3	1.50– 3.90	0.62– 0.85		0.83– 0.97		330	8.00	2057	25.0
12	SEEDS-2	18.4	-5.72			36.1		370	-6.00		
13	LOHAFEX	20.0	-2.50	1.30	-0.20	0.50– 1.40		357.5	-(15–7)		

Sources are as follow: Martin et al., 1994; Steinberg et al., 1998; Boyd et al., 2000; Bakker et al., 2001; Frew et al., 2001; Bakker et al., 2005; Hiscock and Millero, 2005; Smetacek et al., 2005; Takeda and Tsuda, 2005; Wong et al., 2006; Boyd et al., 2007; Tsumune et al., 2009; Harvey et al., 2010; Smetacek and Naqvi, 2010; Berg et al., 2011; Currie et al., 2011; Law et al., 2011.

Table 2. Changes of chemical parameters from initial to after concentrations by OIF experiments. Note that *ΔDIC represents changes in DIC concentrations (i.e., [DIC]_{post-fertilization} – [DIC]_{pre-fertilization}).

-	Experiment	Initial– NO ₃ (μM)	After– NO ₃ (μM)	Initial– PO ₄ (μM)	After– PO ₄ (μM)	Initial– Si (μM)	After– Si (μM)	Initial– pCO ₂ (ppm)	After– pCO ₂ (ppm)	*ΔDIC (μM)
1	IronEx-1	10.8	10.1	0.92	0.90	3.9	3.88	471	458	-6
2	IronEx-2	10.4	6.4	0.80	0.55	5.1	1.1	538	465	-27
3	SOIREE	25.0	22.0	1.50	-	10.0	7.0	350	312–318	-(18–15)
4	EisenEx	22.0	21.0	1.60	1.5	10.0	10.0	360	340–342	-(15–12)
5	SEEDS-1	18.5	2.7	-	0.44	31.8	5.0	390	260	-58

6	SOFEX-N	21.9	20.5	1.40	1.31	2.5	1.4	367	341	-13
7	SOFEX-S	26.3	22.8	1.87	1.66	62.8	58.8	365	329	-21
8	SERIES	10.0-12.0	3.0	>1.00	<0.50	14.0-16.0	<2.0	350	265	-36
9	EIFEX	25.0	23.5	1.80	1.50	19.0	8.0	360	330	-13.5
10	FeeP	<0.01	-	0.01	-	-	-	-	-	<-1
11	SAGE	7.9-10.3	11.8	0.62-0.85	-	0.83-0.97	-	330	338	-25
12	SEEDS-2	18.4	12.7	-	-	36.1	-	370	364	-
13	LOHAFEX	20.0	17.5	1.30	1.10	0.50-1.40	-	-	-	-

Sources are as follow: Martin et al., 1994; Steinberg et al., 1998; Boyd et al., 2000; Bakker et al., 2001; Bakker et al., 2005; Hiscock and Millero, 2005; Smetacek et al., 2005; Takeda and Tsuda, 2005; Wong et al., 2006; Boyd et al., 2007; Tsumune et al., 2009; Harvey et al., 2010; Smetacek and Naqvi, 2010; Berg et al., 2011; Currie et al., 2011; Law et al., 2011.

Table 34. Changes of biological parameters from initial to after (maximum) concentrations by OIF experiments. Note that *PP (mg C m⁻² d⁻¹) was estimated by multiplying PP (mg C m⁻³ d⁻¹) with mixed layer depth (m).

	Experiment	Initial Fv/Fm	Maximum Fv/Fm	Initial Chlorophyll (mg m ⁻³)	Maximum Chlorophyll (mg m ⁻³)	Initial PP (mg C m ⁻² d ⁻¹)	Maximum PP (mg C m ⁻² d ⁻¹)
1	IronEx-1	0.30	0.60	0.24	0.65	300–450*	805–1330*
2	IronEx-2	0.25	0.50	0.15–0.20	4.00	630	2430
3	SOIREE	0.22	0.65	0.25	2.00	120	1300
4	EisenEx	0.30	0.56	0.50	2.50	130–220	790
5	SEEDS-1	0.19	0.31	0.80–0.90	21.8	420	1670
6	SOFEX-N	0.20	0.5	0.15	2.60	144	1500
7	SOFEX-S	0.25	0.65	0.30	3.80	216	972
8	SERIES	0.24	0.55	0.35	5.00	300	2000
9	EIFEX	0.28	0.6	0.70	3.16	750	1500
10	FeeP			0.04	0.07		
11	SAGE	0.27	0.61	0.63	1.33	540	900
12	SEEDS-2	0.29	0.40	0.80	2.48	390	1000
13	LOHAFEX	0.33	0.40–0.50	0.50	1.25	960	1560

Sources are as follow: Kolber et al., 1994; Martin et al., 1994; Behrenfeld et al., 1996; Steinberg et al., 1998; Boyd et al., 2000; Boyd and Law, 2001; Gervais et al., 2002; Coale et al., 2004; Boyd et al., 2005; de Baar et al., 2005; Takeda and Tsuda, 2005; Tsuda et al., 2005; Assmy et al., 2007; Boyd et al., 2007; Tsuda et al., 2007; Kudo et al., 2009; Harvey et al., 2010; Berg et al., 2011; Currie et al., 2011; Peloquin et al., 2011; Smetacek et al., 2012; Thiele et al., 2012; Martin et al., 2013; Latasa et al., 2014.

Table 5. Export flux ($\text{mg C m}^{-2} \text{ d}^{-1}$); initial and maximum values in patch at each depth (measurement day from the beginning of OIF experiment), initial and maximum values outside patch at each depth (measurement day from the beginning of OIF experiment), measurement depth, measurement method, and method description to detect enhanced export production.

Experiment	In patch Initial (day)	In patch Maximum (day)	Outside Initial (day)	Outside Maximum (day)	Depth (m)	Method	Method description
1 IronEx-1							
2 IronEx-2	84 (0)	600 (7)			25	^{234}Th	*Water column at 0, 25 m (^{234}Th , $^{13}\text{C}_{\text{org}}$)
							*Water column in the upper 100 m (^{234}Th , $^{13}\text{C}_{\text{org}}$)
3 SOIREE	146/73 (0)	193/74 (11)	146/73 (0)	78/38 (11)	110/310	^{234}Th , trap	*Free-drifting sediment traps at 110, 310 m (^{234}Th , $^{13}\text{C}_{\text{org}}$, total mass, POC, biogenic silica (BSi), particulate organic nitrogen (PON))
							*Transmissometer
4 EisenEx							*Water column (^{234}Th)
							*Sediment trap at 20, 500, 3500 m (POC)
5 SEEDS-1	374/166 (2)	1000/140 (13)			50/200	^{234}Th , trap	*Water column in the upper 200 m (POC, PON, BSi, ^{234}Th)
							*Drifting sediment trap at 40, 60, 100, 200 m (POC, PON, BSi, ^{234}Th)
6 SOFeX-N							*Autonomous floats profiling transmissometer
7 SOFeX-S	36/19 (6)	112/142 (27)	48/38 (7)	49/56 (27)	50/100	^{234}Th	*Water column (^{234}Th , POC)
							*Water column at 25, 50, 75, 100, 125 m (^{234}Th , POC, PON, BSi)
8 SERIES	120/48 (3)	480/192 (24)	192 (3)	139 (15)	50/100	^{234}Th , trap	*Water column in the upper 110 m (POC, BSi)
							*Free-drifting sediment traps at 100 and 300 m (POC, BSi, ^{234}Th)
							*Transmissometer
9 EIFEX	340 (0)	1692 (32)	396 (0)	516 (32)	100	^{234}Th	*Sediment trap in the 1000 m upper layer (BSi, POC, PON, ^{234}Th , $^{13}\text{C}_{\text{org}}$, PON, stable nitrogen isotope of PON ($^{15}\text{N}_{\text{PON}}$))
10 FeeP							
11 SAGE							*Free-drifting sediment traps at 80, 300 m (POC, PON, BSi)
							*Particle camera deployments
12 SEEDS-2	290/316 (1-4)	580/336 (19-22)	299/212 (1-8)	509/204 (18-31)	40/100	Trap	*Water column in the upper 100 m (POC, PON, BSi, $^{13}\text{C}_{\text{org}}$)
							*Drifting sediment trap at 40, 70, 100 m (POC, PON, BSi, $^{13}\text{C}_{\text{org}}$)
							*Neutrally buoyant sediment traps at 200, 450 m (POC, PON, ^{234}Th)
13 LOHAFEX	60 (0)	94 (23)	78 (4)	97 (25)	100	^{234}Th	*Underwater video profiler
							*Water column in the upper 100 m (POC, PON, ^{234}Th)

Sources are as follow: Bidigare et al., 1999; Nodder et al., 2001; Nodder and Waite, 2001; Trull and Armand, 2001; Waite and Nodder, 2001; Bishop et al., 2004; Boyd et al., 2004; Buesseler et al., 2004; Coale et al., 2004; Aono et al., 2005; Takeda and Tsuda, 2005; Tsuda et al., 2007; Jacquet et al., 2008; Aramaki et al., 2009; Peloquin et al., 2011; Smetacek et al., 2012; Martin et al., 2013.

Figure Captions

Fig. 1. Diagram showing the monthly atmospheric CO₂ concentrations (ppm) (blue) according to the Mauna Loa Observatory, Hawaii (<http://www.esrl.noaa.gov/gmd/ccgg/trends/data.html>), global monthly land surface air and sea surface temperature anomalies (°C) (red) (<http://data.giss.nasa.gov/gistemp/>), and pH (green) measured at station ALOHA in the central Pacific (http://hahana.soest.hawaii.edu/hot/products/HOT_surface_CO2.txt). The data values represent moving average values for 12 months and shading indicates the standard deviation of 12 months.

Fig. 2. Schematic representation of several proposed climate-engineering methods (modified from Matthews, 1996).

Fig. 3. The iron hypothesis as suggested by Martin (1990). (a) Efficiency of the biological pump under normal conditions and (b) efficiency of the biological pump as a result of Fe enrichment. DIC is dissolved inorganic carbon and OM is organic matter (modified from Sarmiento and Gruber, 2006).

Fig. 4. Global annual distribution of surface (a) chlorophyll concentrations (mg m⁻³), (b) nitrate concentrations (μM), and (c) silicate concentrations (μM). Chlorophyll-a concentration distribution represents the Aqua MODIS chlorophyll-a composite from July 2002 to February 2016 (<http://oceancolor.gsfc.nasa.gov/cgi/l3>), while ~~the nitrate and silicate were plotted the nitrate and silicate distributions were presented~~ by Ocean Data View program (<https://odv.awi.de>) using the World Ocean Atlas 2013 dataset (https://odv.awi.de/en/data/ocean/world_ocean_atlas_2013). White circles indicate the locations of 13 artificial OIF experiments and black triangles indicate the locations of natural OIF experiments. Note that the numbers indicate the order of experiments (see Table 1).

Fig. 5. ~~Photographs of iron the addition procedure. Panels a-e taken during EIFEX and LOHAFEX. Pictures for iron addition procedures: (a) Iron (II) sulfate bags Iron(II) sulfate of 7000 kg, (b) the funnel where iron and hydrochloric acid were poured hydrochloric acid, (c) tank system for mixing with Iron(II) sulfate, hydrochloric acid, and seawater, (d) outlet pipe connected with tank system, (e) pumping iron into prop wash during EIFEX (Smetacek, 2015).-(f) Discharging of Iron(II) sulfate (<http://www.geoengineeringmonitor.org/reasons-to-oppose/>).~~

Fig. 6. (a) Patch size (km²) for first Fe addition (blue bar) and maximum patch size (sky blue bar) during OIF experiments. (b) Amounts (kg) of first Fe addition (blue bar) and total Fe addition (sky blue bar). (c) Minimum (blue bar) and maximum (sky blue bar) mixed layer depth (m). (d) Average sea surface temperature (°C). Initial (e) nitrate concentrations (μM), (f) silicate concentrations (μM), (g) Fv/Fm ratio, and (h) chlorophyll-a concentrations (mg m⁻³) before iron addition. Note that the numbers indicate the order of experiments (see Table 1). Sources are as follows: Kolber et al., (1994); Martin et al., (1994); Behrenfeld et al., (1996); Coale et al., (1996); Steinberg et al., (1998); Boyd et al., (2000); Boyd and Law, (2001); Gervais et al., (2002); Coale et al., (2004); Boyd et al., (2004); Boyd et al., (2005); de Baar et al., (2005); Hiscock and Millero, (2005); Takeda and Tsuda, (2005); Tsuda et al., (2005); Assmy et al., (2007); Boyd et al., (2007); Tsuda et al., (2007); Harvey et al., (2010); Berg et al., (2011); Law et al., (2011); Peloquin et al., (2011); Smetacek et al., (2012); Thiele et al., (2012); Martin et al., (2013); Latasa et al., (2014).

Fig. 7. (a) Initial (coral bar) and maximum (light coral bar) Fv/Fm ratio during OIF experiments. (b) Changes in nitrate concentrations ($\Delta\text{Nitrate} = [\text{NO}_3^-]_{\text{post-fertilization}} - [\text{NO}_3^-]_{\text{pre-fertilization}}$; μM). (c) Initial (coral bar) and maximum (light coral bar) chlorophyll-a concentrations (mg m⁻³). (d) Distributions of chlorophyll-a concentrations (mg m⁻³) at ~28 days after iron addition in the SOFeX-N and at ~20 days in the SOFeX-S. White dotted box indicates phytoplankton bloom during OIF experiments. Changes in (e) primary productivity ($\Delta\text{PP} = [\text{PP}]_{\text{post-fertilization}} - [\text{PP}]_{\text{pre-fertilization}}$; mg C m⁻² d⁻¹) and in (f) pCO₂ ($\Delta p\text{CO}_2 = [p\text{CO}_2]_{\text{post-fertilization}} - [p\text{CO}_2]_{\text{pre-fertilization}}$; ppm). Color bar indicates changes in DIC ($\Delta\text{DIC} = [\text{DIC}]_{\text{post-fertilization}} - [\text{DIC}]_{\text{pre-fertilization}}$; μM). Note that PP (mg C m⁻² d⁻¹) of OIF experiment number 1 (IronEx-1) was estimated by multiplying PP (mg C m⁻³ d⁻¹) with mixed layer depth and the numbers indicate the order of experiments (see Table 1). Sources are as follows: Kolber et al., (1994); Martin et al., (1994); Behrenfeld et al., (1996); Coale et al., (1996); Steinberg et al., (1998); Boyd et al., (2000); Bakker et al., (2001); Boyd and Law, (2001); Gervais et al., (2002); Coale et al., (2004); Boyd et al., (2004); Bakker et al., (2005); Boyd et al., (2005); de Baar et al., (2005); Hiscock and Millero, (2005); Smetacek et al., (2005); Takeda and Tsuda, (2005); Tsuda et al., (2005); Wong et al., (2006); Assmy et al., (2007); Boyd et al., (2007); Tsuda et al., (2007); Kudo et al., (2009); Tsumune et al., (2009); Harvey et al., (2010); Smetacek and Naqvi, (2010); Berg et al., (2011); Currie et al., (2011); Law et al., (2011); Peloquin et al., (2011); Smetacek et al., (2012); Thiele et al., (2012); Martin et al., (2013); Latasa et al., (2014).

Fig. 8. Time-series of (a) ²³⁴Th-derived particulate organic carbon (POC) fluxes (mg m⁻² d⁻¹) of the upper 100 m layer in patch (coral bar) and outside patch (blue bar) during EIFEX (modified from Smetacek et al., 2012). Time-series of (b) vertically

integrated ^{234}Th (dpm l^{-1}) in patch (coral circle) and outside patch (blue diamond) relative to parent ^{238}U (dpm l^{-1} ; dotted black line) during SOIREE (modified from Nodder et al., 2001).

Fig. 9. Assessment framework for scientific research involving ocean fertilization (OF) (modified from Assessment Framework for Scientific Research Involving Ocean Fertilization, 2010).

(a) Time-series of mixed layer depth-integrated chlorophyll-a concentrations (mg m^{-2}) during SOIREE (pink line), SEEDS-1 (brown line), SERIES (cyan line), SEEDS-2 (blue line), and EIFEX (teal line). Sources are as follows: Boyd and Abraham, (2001); Tsuda et al., (2007); Assmy et al., (2013). (b) The distributions of chlorophyll-a concentrations (mg m^{-3}) in ~5 days and ~46 days during SOIREE from SeaWiFS Level-2 daily images.

Fig. 10. (a) Time-series of mixed layer depth-integrated chlorophyll-a concentrations (mg m^{-2}) during SOIREE (pink line), SEEDS-1 (brown line), SERIES (cyan line), SEEDS-2 (blue line), and EIFEX (teal line). Sources are as follows: Boyd and Abraham, (2001); Tsuda et al., (2007); Assmy et al., (2013). (b) The distributions of chlorophyll-a concentrations (mg m^{-3}) in ~5 days and ~46 days during SOIREE from SeaWiFS Level-2 daily images. ~~Assessment framework for scientific research involving ocean fertilization (OF) (modified from Assessment Framework for Scientific Research Involving Ocean Fertilization, 2010).~~

Fig. 11. Schematic diagram of KIFES representing experiment target site (eddy structure) and survey methods (underway sampling systems, multiple sediment traps, sub-bottom profilers, sediment coring systems, and satellite observations).

Fig. 1

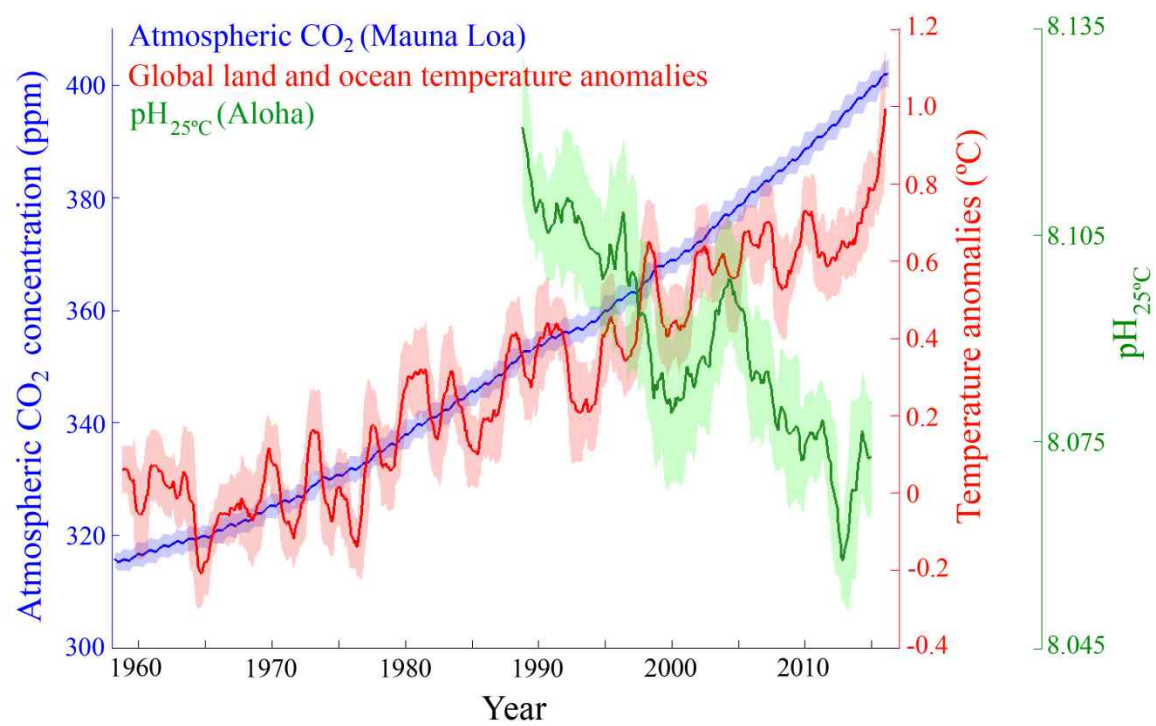


Fig. 2

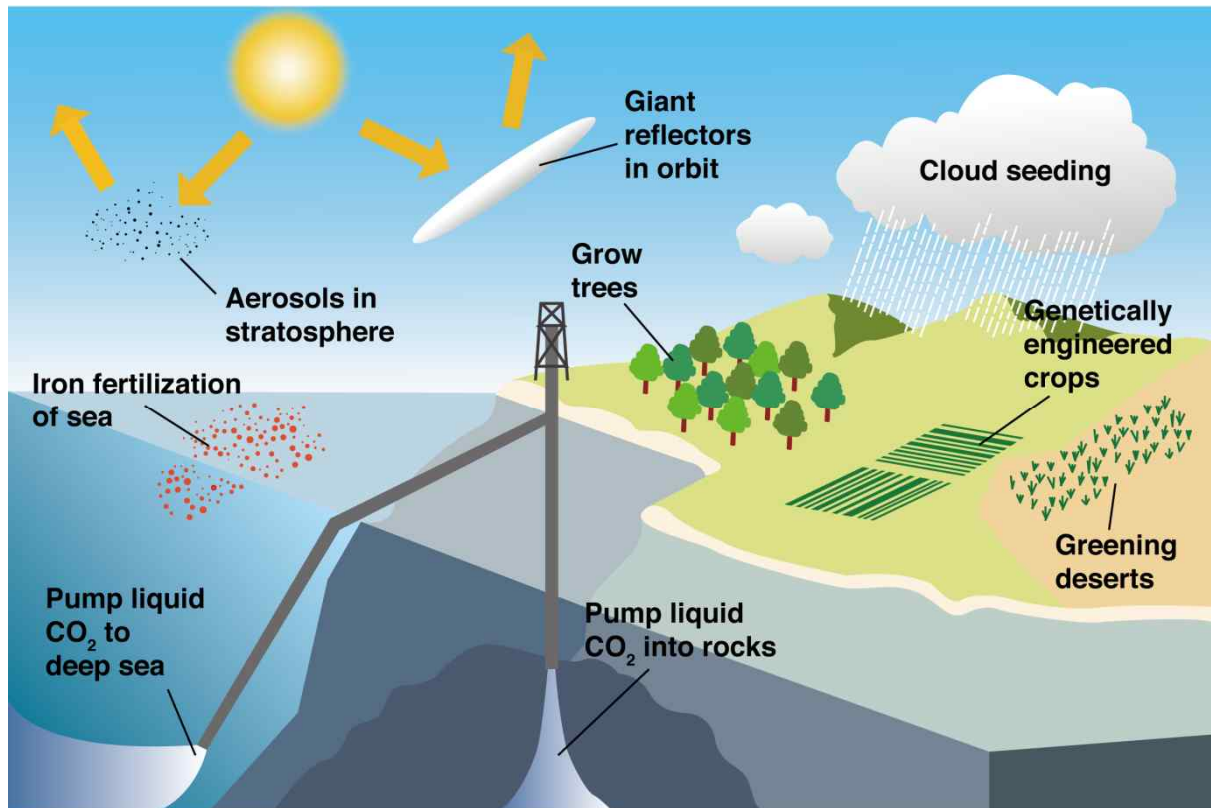


Fig. 3

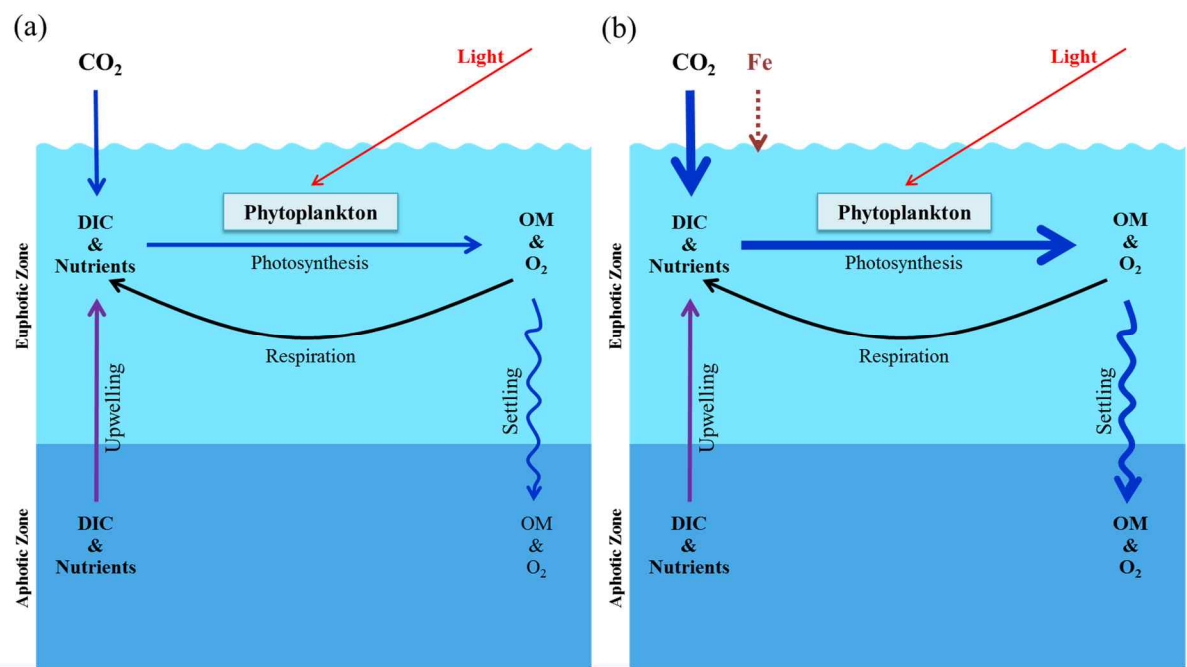
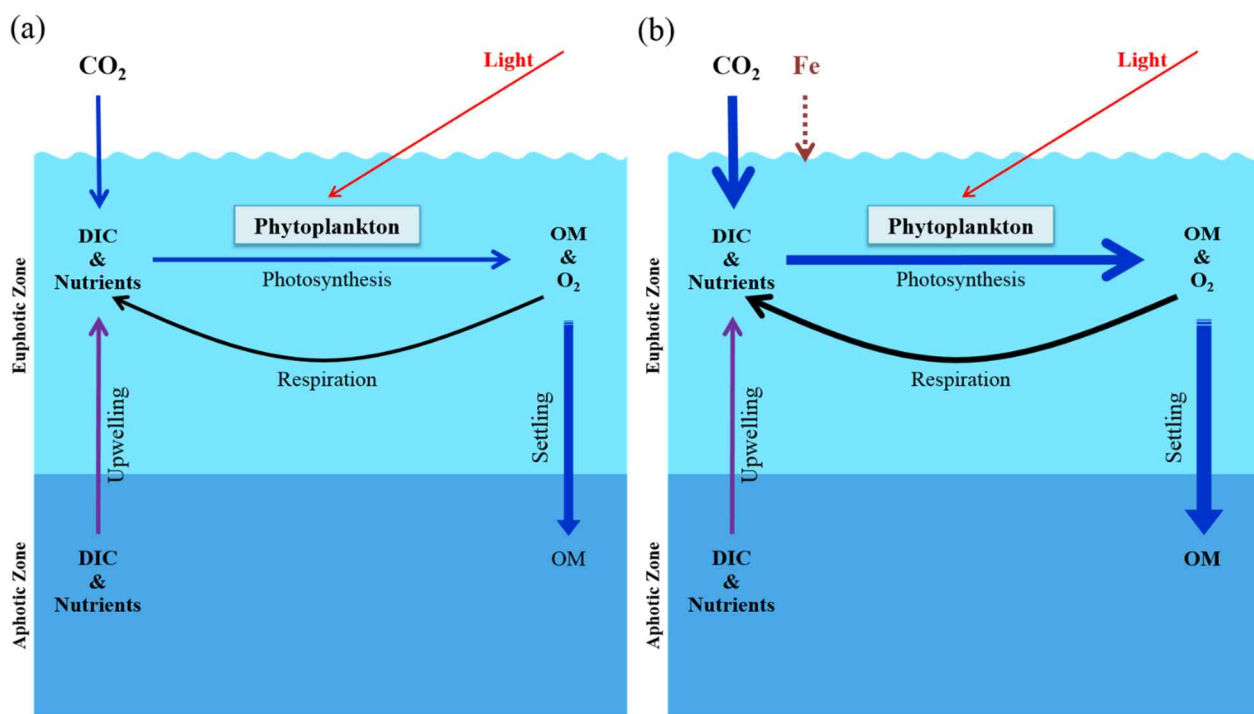
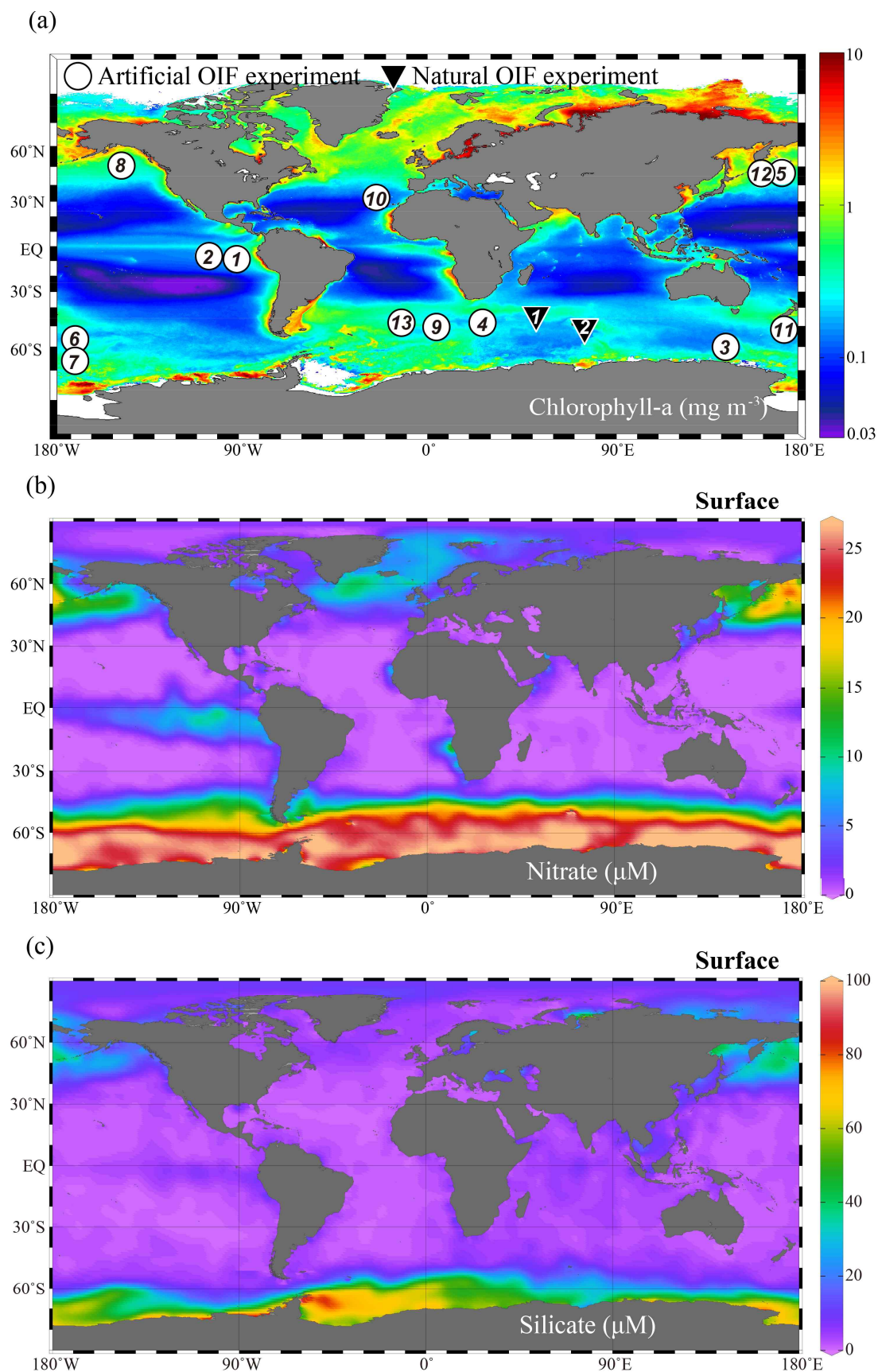


Fig. 4





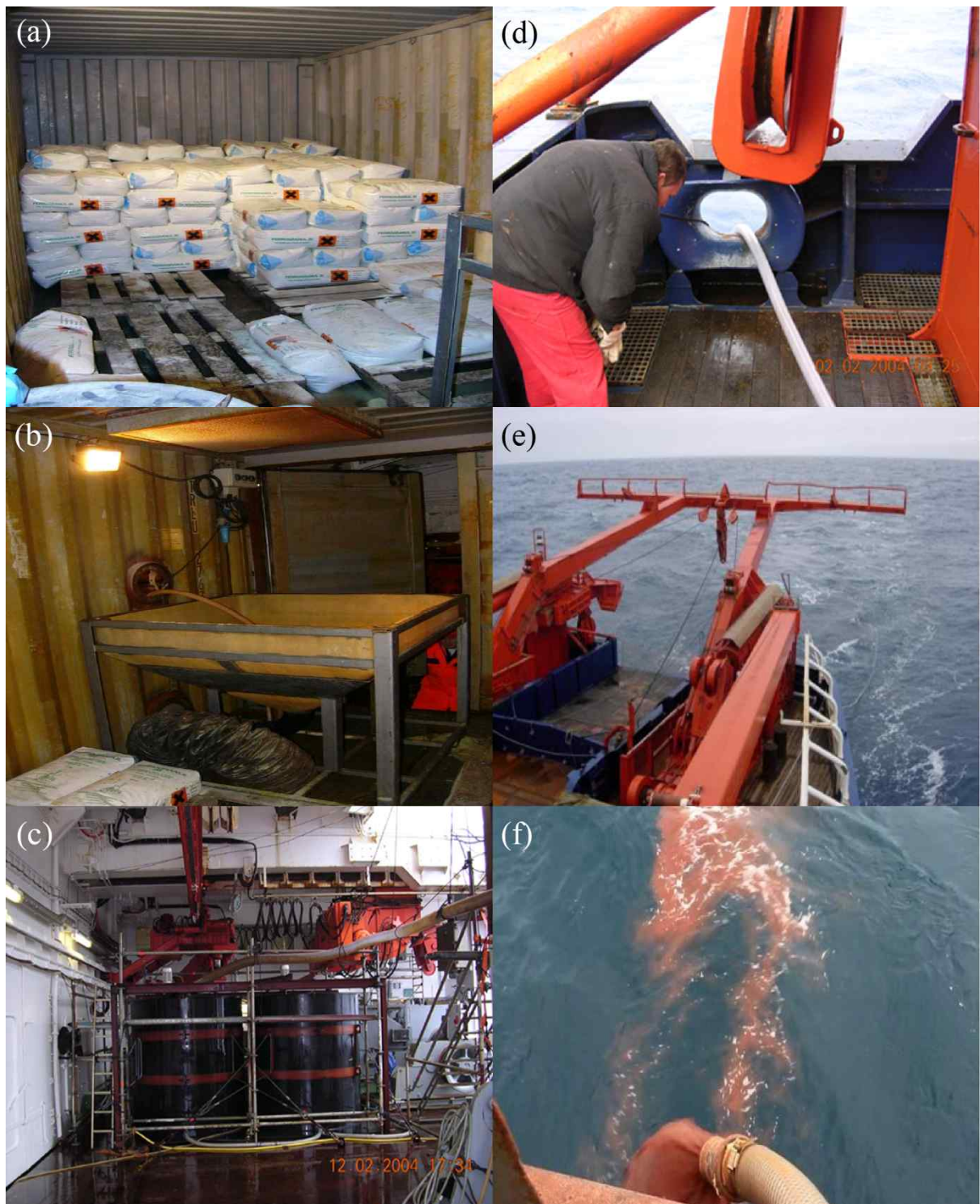


Fig. 6

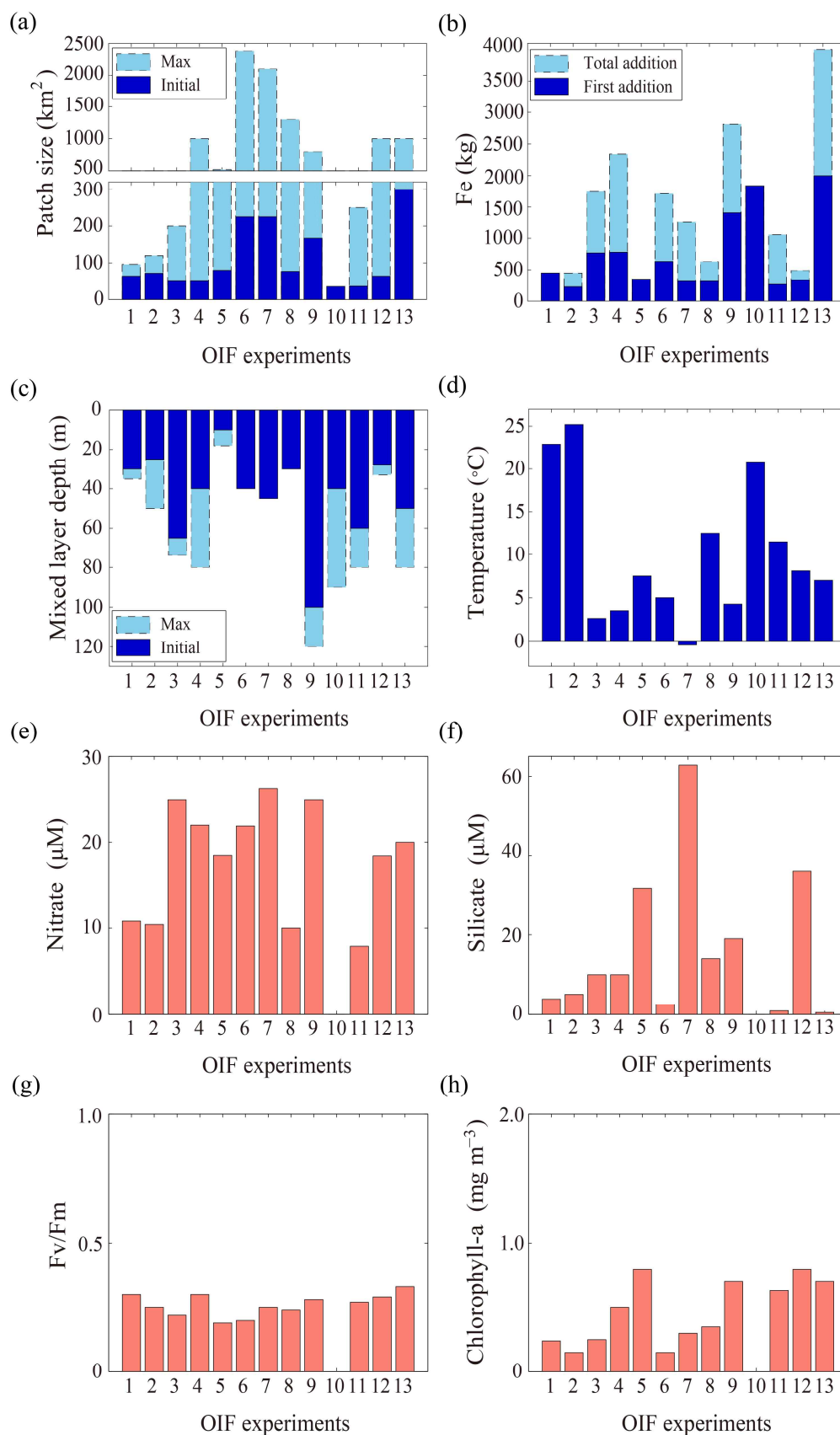
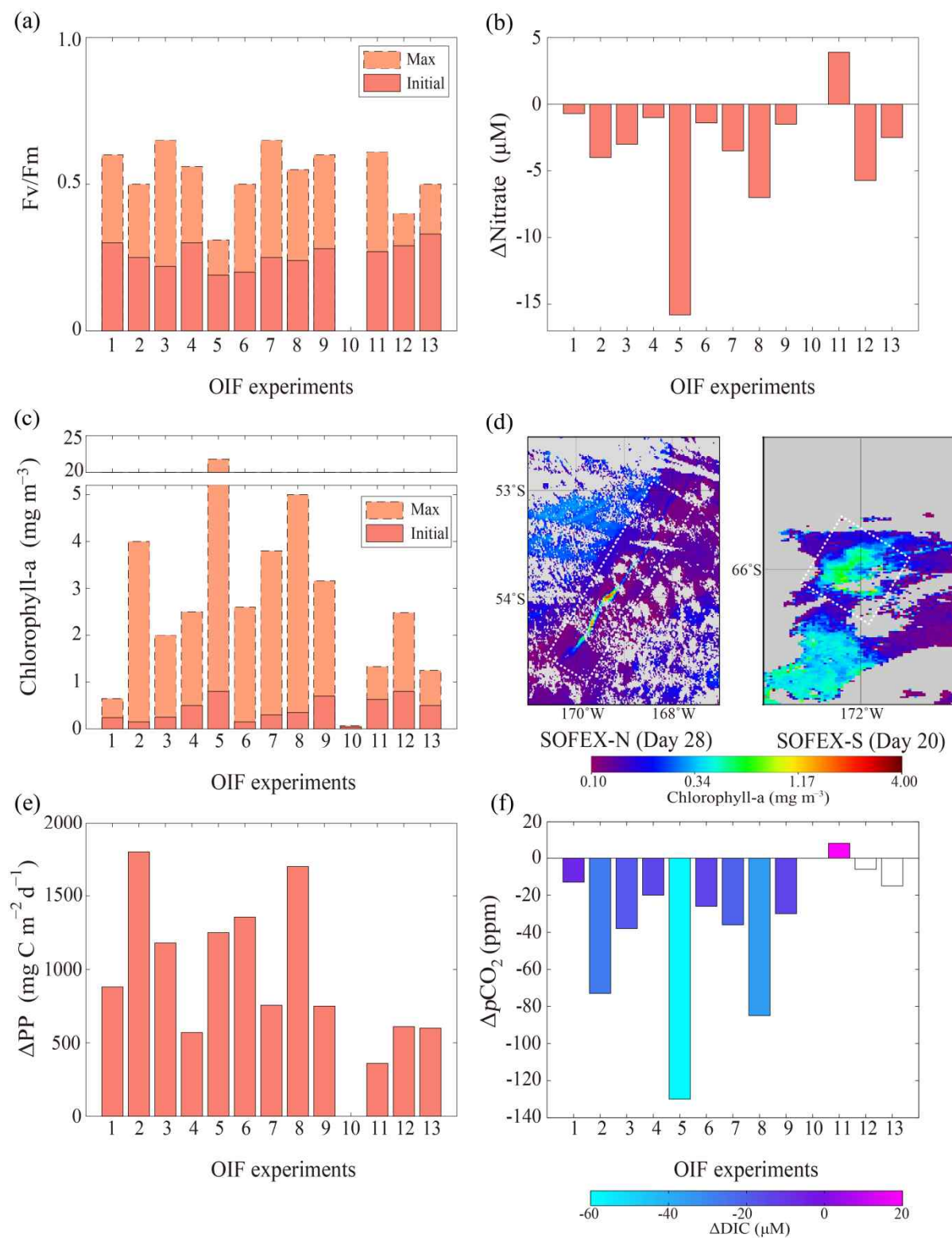
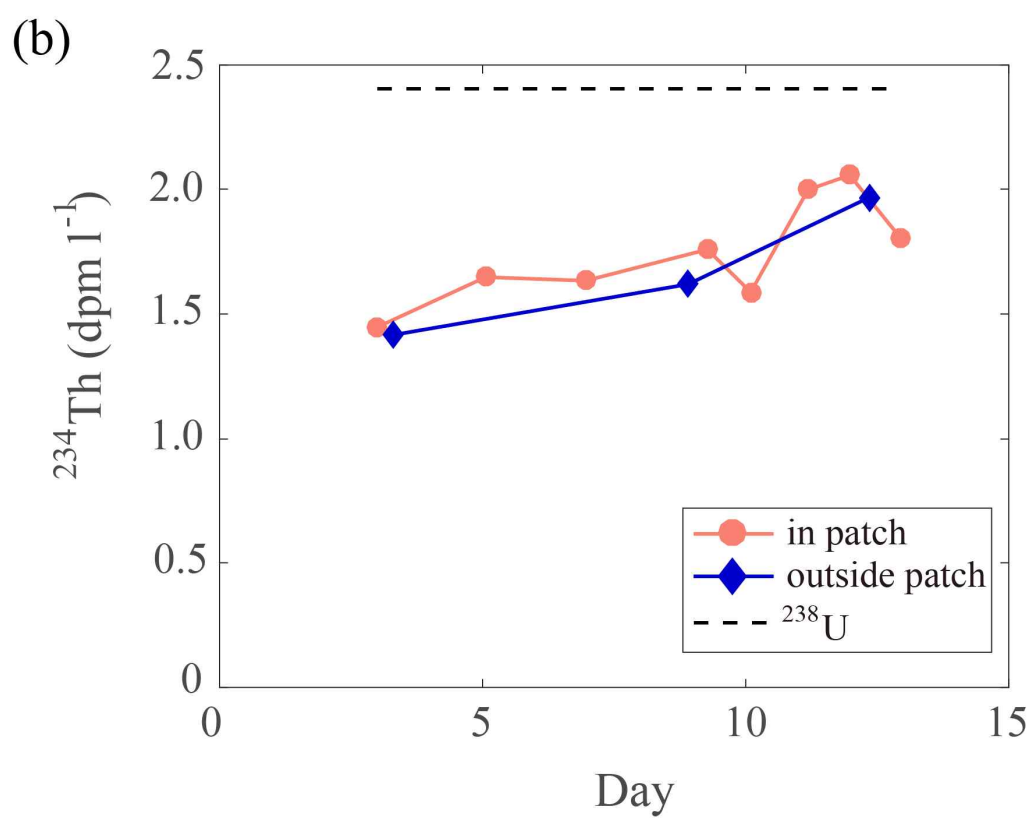
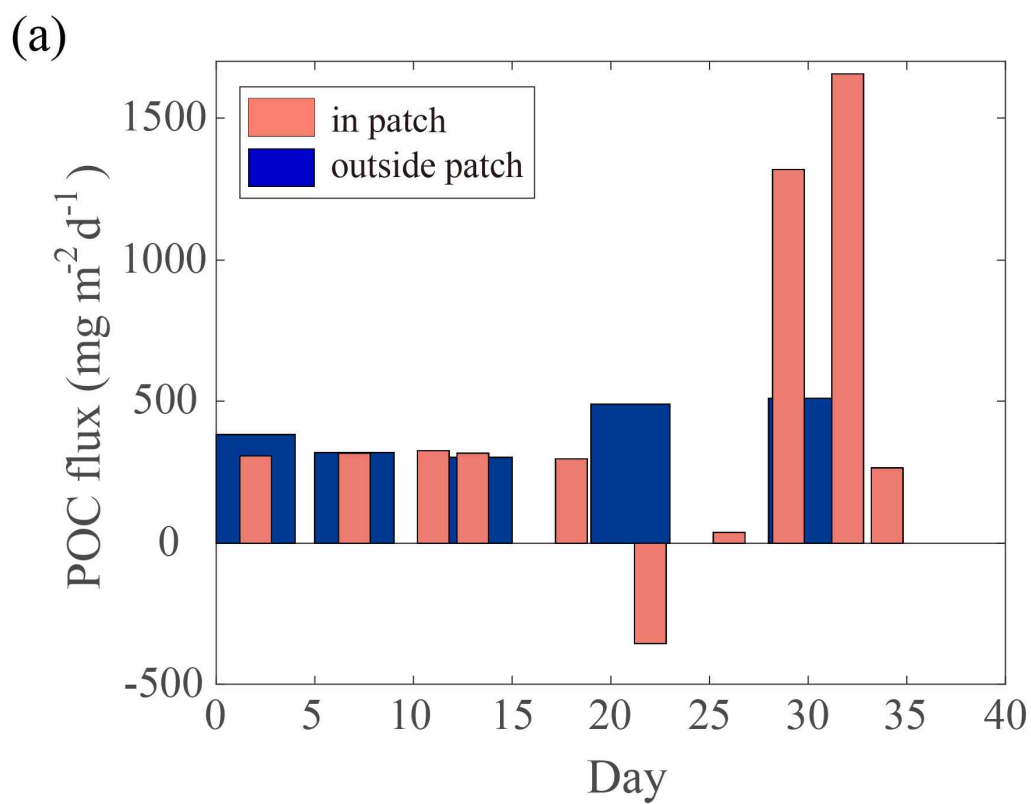
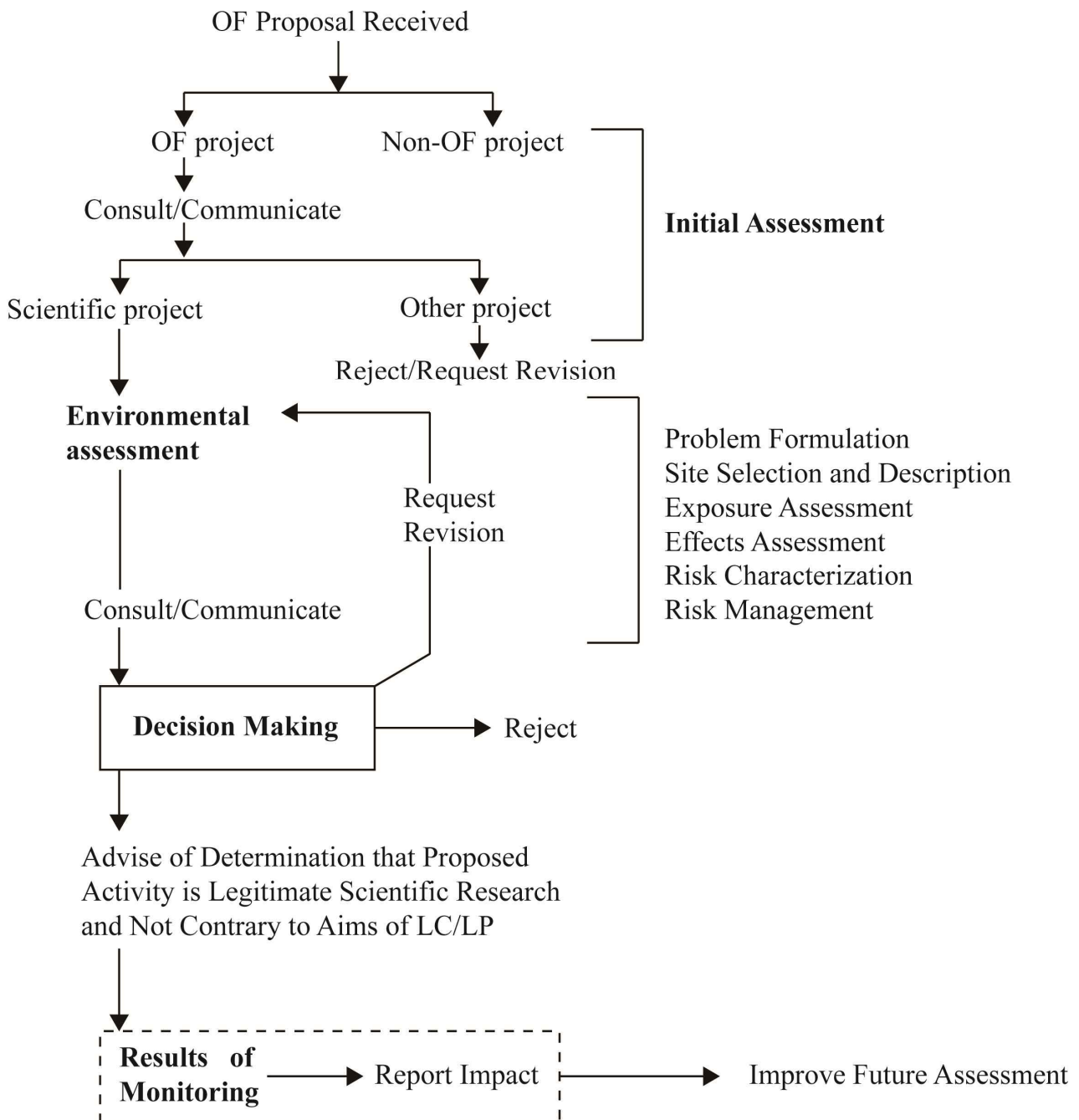
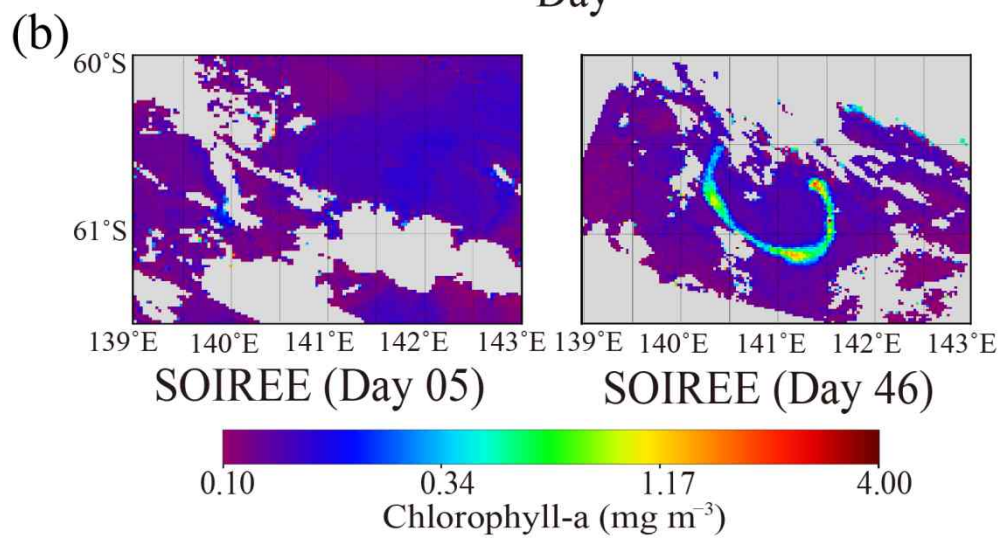
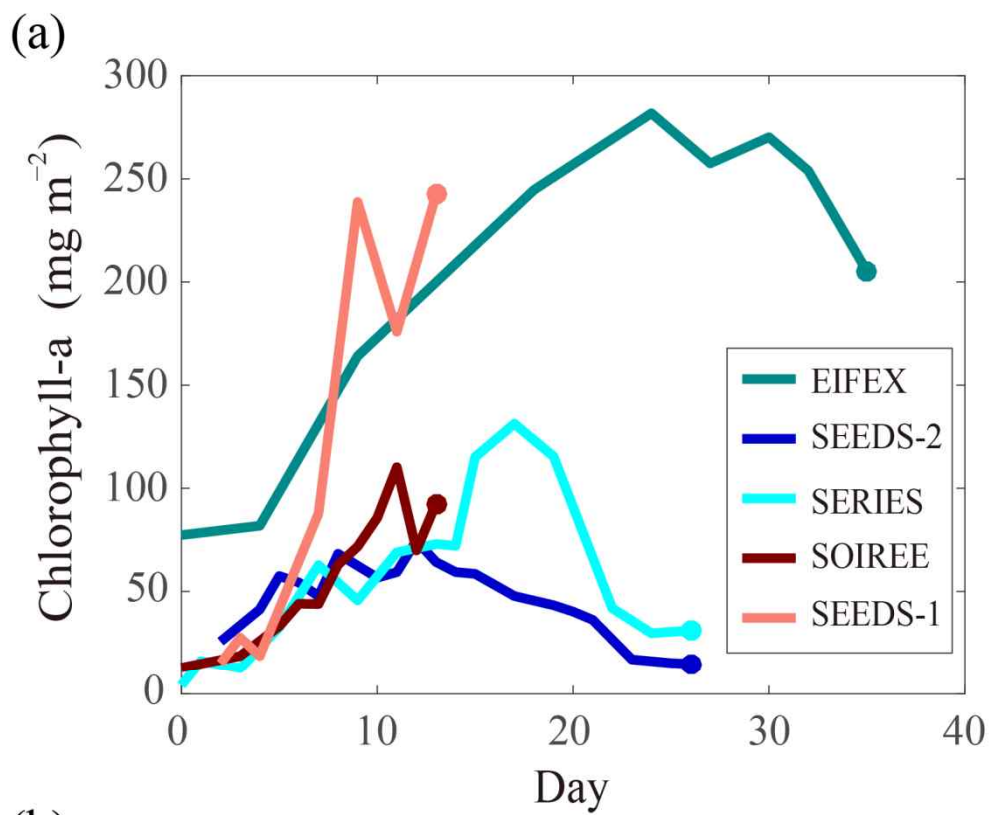


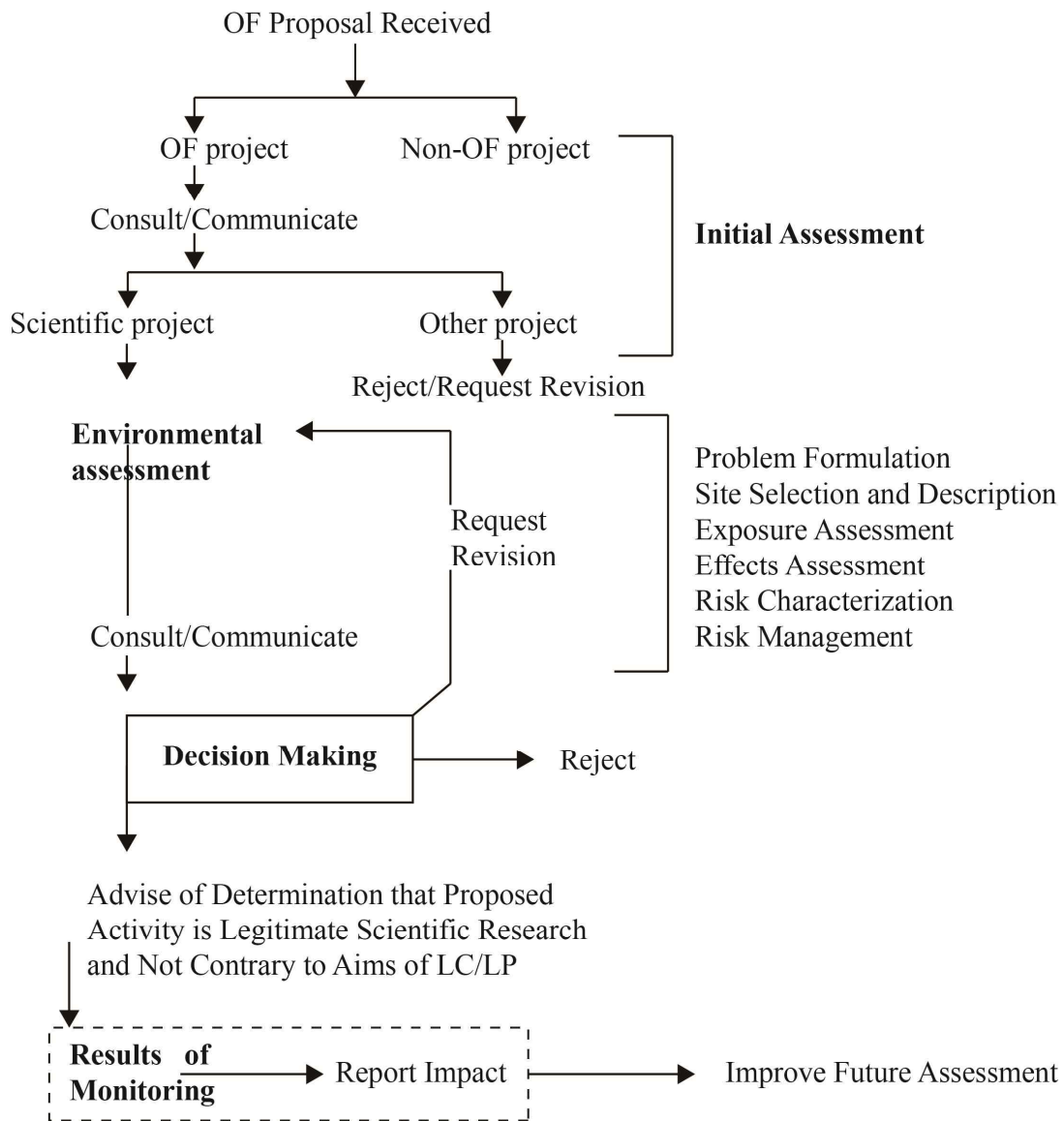
Fig. 7











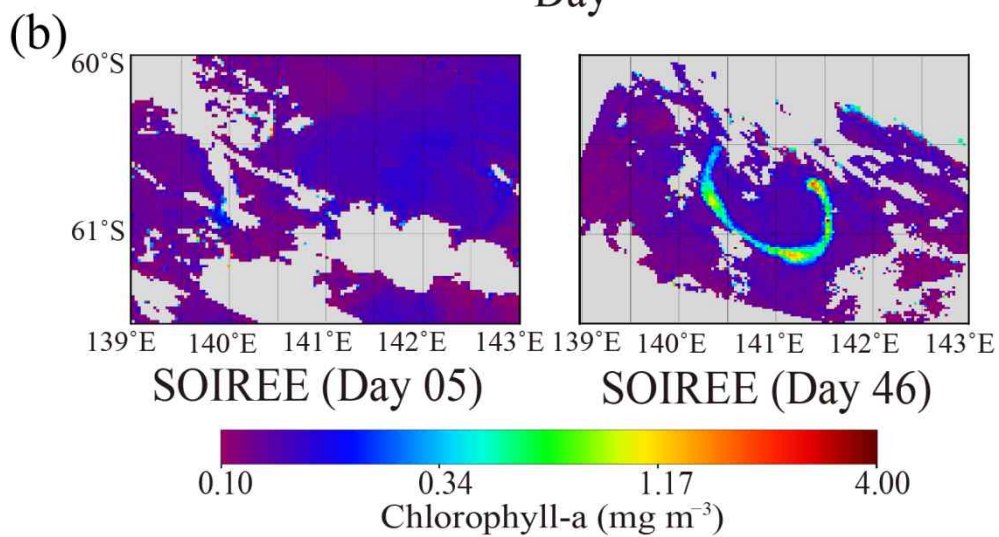
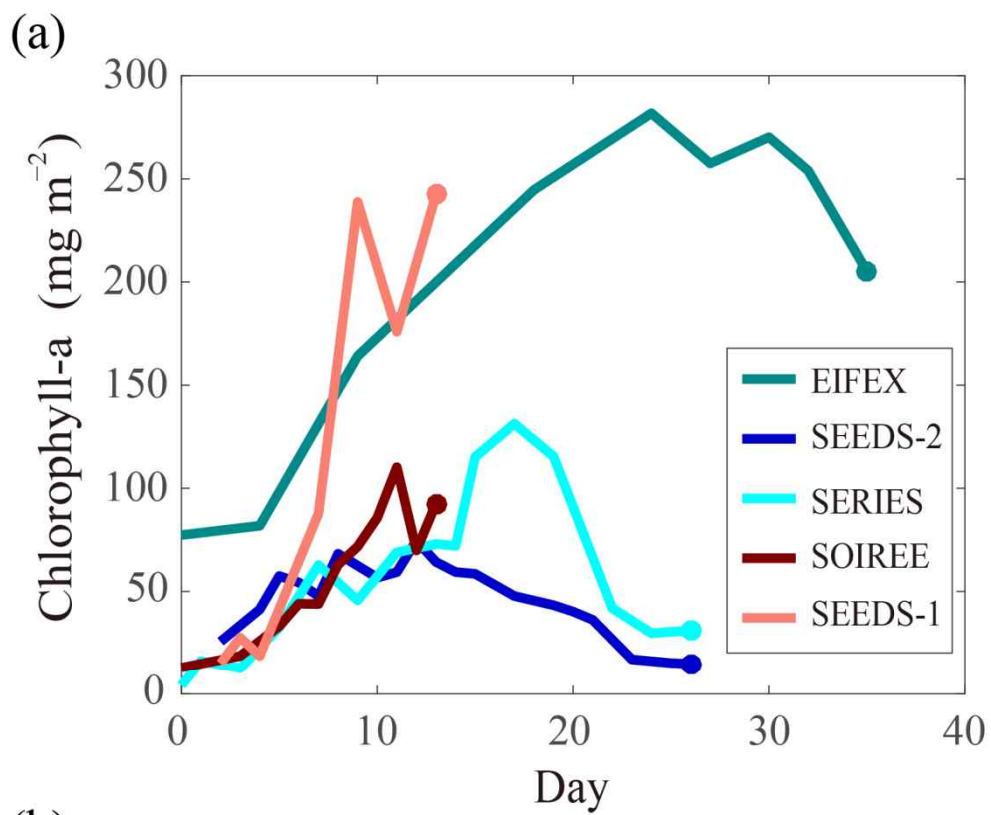


Fig. 11

