



# Predicting and monitoring the effects of large-scale ocean iron fertilization on marine trace gas emissions

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**ABSTRACT:** Large-scale (>40 000 km<sup>2</sup>, >1 yr) ocean iron fertilization (OIF) is being considered as an option for mitigating the increase in atmospheric CO<sub>2</sub> concentrations. However OIF will influence trace gas production and atmospheric emissions, with consequences over broad temporal and spatial scales. To illustrate this, the response of nitrous oxide (N<sub>2</sub>O) and dimethylsulphide (DMS) in the mesoscale iron addition experiments (FeAXs) and model scenarios of large-scale OIF are examined. FeAXs have shown negligible to minor increases in N<sub>2</sub>O production, whereas models of long-term OIF suggest significant N<sub>2</sub>O production with the potential to offset the benefit gained by iron-mediated increases in CO<sub>2</sub> uptake. N<sub>2</sub>O production and emission will be influenced by the magnitude and rate of vertical particle export, and along-isopycnal N<sub>2</sub>O transport will necessitate monitoring over large spatial scales. The N<sub>2</sub>O–O<sub>2</sub> relationship provides a monitoring option using oxygen as a proxy, with spatial coverage by Argo and glider-mounted oxygen optodes. Although the initial FeAXs exhibited similar increases (1.5- to 1.6-fold) in DMS, a subsequent sub-arctic Pacific experiment observed DMS consumption relative to unfertilized waters, highlighting regional variability as a complicating factor when predicting the effects of large-scale OIF. DMS cycling and its influence on atmospheric composition may be studied using naturally occurring blooms and be constrained prior to OIF by pre-fertilization spatial mapping and aerial sampling using new technologies. As trace gases may have positive or negative synergistic effects on atmospheric chemistry and climate forcing, the net effect of altered trace gas emissions needs to be considered in both models and monitoring of large-scale OIF.

**KEY WORDS:** Iron fertilization · Trace gases · Nitrous oxide · Dimethylsulphide · Remineralization

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## INTRODUCTION

Enhancing ocean productivity and vertical carbon export by increasing iron supply will indirectly influence the production of a range of trace gases, often via a complex web of biogeochemical interactions. The resulting change in oceanic emissions may alter atmospheric composition with positive or negative feedbacks on radiative forcing, tropospheric oxidation capacity and ozone concentration (Liss et al. 2005). However, the response of oceanic trace gas emissions to iron fertilization is currently uncertain, primarily as indirect effects and biogeochemical feedbacks have received limited attention in the 12 mesoscale iron addition experiments (FeAXs) to date (Boyd et al. 2007). This is a reflection of the priority of FeAXs to test the 'iron hypothesis' (Martin 1990) by focussing on phytoplankton productivity

and carbon export and of the relatively short-term nature and scale of FeAXs relative to the temporal and spatial scales of trace-gas cycling. For example, dimethylsulphide (DMS), non-methane hydrocarbons and halocarbons are influenced during the phytoplankton growth phase and generally show a short-term response in the surface mixed layer within days to weeks; conversely, production of trace gases that are influenced by remineralization of sinking particulate matter during the bloom decline and export phase occurs over greater temporal and spatial scales (Fig. 1). With the current consideration of large-scale ocean iron fertilization (OIF) (here defined as continuous fertilization over areas >40 000 km<sup>2</sup> for periods of >1 yr) as a strategy for lowering atmospheric CO<sub>2</sub>, there is a need to consider potential trace-gas responses, using FeAX observations, natural analogues and model scenarios, for pre-

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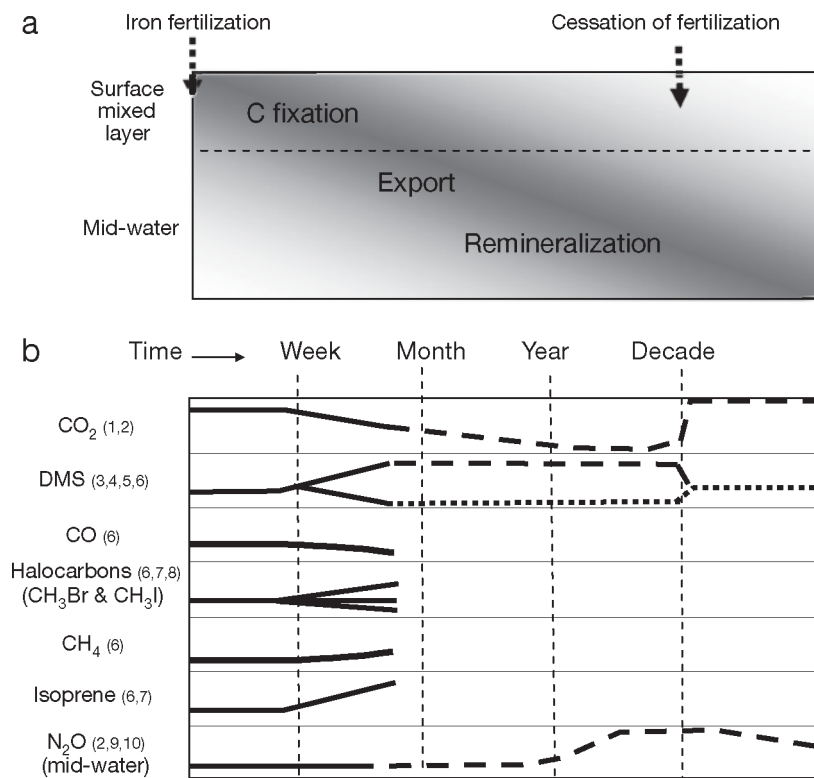


Fig. 1. (a) Conceptual response to iron fertilization showing the temporal evolution from carbon fixation during the bloom phase to remineralization in the mid-water column, with cessation of iron fertilization after 10 yr. (b) Temporal response of CO<sub>2</sub> and trace gases in surface waters and N<sub>2</sub>O in the mid-water column based on the FeAX observations (solid lines) and model output and extrapolations (dashed and dotted lines) of (1) Wong et al. (2006), (2) Jin & Gruber (2003), (3) Turner et al. (2004), (4) Takeda & Tsuda (2005), (5) Levasseur et al. (2006) (observed DMS results extrapolated as dotted line), (6) Wingenter et al. (2004) (observed DMS results extrapolated as dashed line), (7) Moore & Wang (2006), (8) Liss et al. (2005), (9) Law & Ling (2001), and (10) Walter et al. (2005)

diction and development of monitoring strategies (London Convention 2007).

### N<sub>2</sub>O RESPONSE TO OIF

Nitrous oxide (N<sub>2</sub>O) is an example of a trace gas that may respond to OIF on greater temporal and spatial scales. The oceans are a major contributor to the global N<sub>2</sub>O budget, providing 5.6 to 14 Tg N yr<sup>-1</sup> (Bange 2006) of the total 7.6 to 41 Tg N yr<sup>-1</sup> (IPCC 2007), primarily from coastal, shelf and upwelling regions. Nitrification is the main source of N<sub>2</sub>O in the open ocean, with the yield increasing with decreasing oxygen (Goreau et al. 1980), as evidenced by an anti-correlation between dissolved N<sub>2</sub>O and oxygen throughout the oceans (Nevison et al. 2003). A N<sub>2</sub>O maximum in intermediate waters is apparent throughout much of the ocean; this maximum shoals and intensifies in upwelling regions, which act as 'natural chimneys' by contributing dispro-

portionately to total marine N<sub>2</sub>O emissions (Law & Owens 1990). Upwelling systems may be regarded as natural large-scale OIF analogues as they are characterized by enhanced vertical particle export. Elevated mid-water remineralization and oxygen consumption not only supports N<sub>2</sub>O production but also leads to anoxia, as observed in the Californian and Namibian coastal upwelling systems (Monteiro et al. 2006, Chan et al. 2008). Denitrification is a minor source but the primary microbial sink for N<sub>2</sub>O and occurs in anoxic sediments and water bodies. As surface and most intermediate waters do not experience hypoxia or contact sediments, N<sub>2</sub>O loss to denitrification will be minimal, so the ultimate fate of this N<sub>2</sub>O is ventilation to the atmosphere. N<sub>2</sub>O is relatively long-lived in the atmosphere and has a global warming potential (GWP) 310 times that of CO<sub>2</sub> (Forster et al. 2007). The potential then exists for N<sub>2</sub>O emissions to offset the radiative decrease achieved by iron-mediated phytoplankton CO<sub>2</sub> uptake and consequently monitoring and verification of N<sub>2</sub>O response should be a priority in any large-scale OIF.

Upscaling of observations from FeAXs to large-scale OIF is limited by the paucity of N<sub>2</sub>O measurements to date. No significant increase in mixed layer N<sub>2</sub>O concentration and emissions was observed on 2 Southern Ocean FeAXs (Law & Ling 2001, Walter et al. 2005); however, an increase in N<sub>2</sub>O saturation of 7% was identified in the upper pycnocline in the Southern Ocean Iron Release Experiment (SOIREE) iron patch that co-varied with column-integrated chlorophyll *a*, suggesting iron-induced stimulation of N<sub>2</sub>O production (Law & Ling 2001). Excess N<sub>2</sub>O was not observed during a subsequent FeAX in the Southern Ocean, the European Iron Fertilization Experiments (EIFEX), although water column sampling was limited and did not focus upon density discontinuities where particles may accumulate (Walter et al. 2005). Measurements during the initial 13 d of the Sub-arctic Ecosystem Response to Iron Enrichment Study (SERIES) FeAX in the Gulf of Alaska identified an increase in N<sub>2</sub>O saturation of 8% at 30 to 50 m (C. Law unpubl. data)—coincident with increases in ammonium and nitrite—suggesting, but not confirming, nitrification as the source. Nitrification in the lower euphotic zone is a significant N<sub>2</sub>O source, contributing

40 to 75 % of atmospheric emissions from the sub-tropical gyres (Dore et al. 1998, Popp et al. 2002). Although generally considered insignificant in surface waters due to light inhibition, nitrification rates have recently been shown to be uniform throughout the surface mixed layer (Yool et al. 2007). These observations indicate the potential for local  $N_2O$  production in surface waters—and hence atmospheric emissions—to increase following OIF on short timescales.

$N_2O$  production is not confined to surface waters, with the rate of vertical particle export determining the subsequent timeframe, magnitude and location of  $N_2O$  emissions. Although few FeAXs have been of sufficient duration to record the export phase (Boyd et al. 2007), those that were, provide a range of findings. Vertical export below the thermocline was relatively insignificant during SERIES due to bacterial remineralization of the diatom bloom in near-surface waters (Boyd et al. 2005), whereas vertical export of a diatom bloom during EIFEX was rapid, with aggregate sinking rates of several hundred  $m\ d^{-1}$  (V. Smetacek pers. comm.). This rapid export to the seafloor may account for the reported absence of  $N_2O$  accumulation below the EIFEX patch (Walter et al. 2005), although the higher and more variable  $N_2O$  concentrations between 500 to 2000 m depth beneath the iron fertilized waters suggest potential  $N_2O$  production. Rapid sinking of particles would limit  $N_2O$  production in the upper water column and maximize the time period before ventilation. Consequently, the vertical particle export rate is critical to OIF, not just in terms of the efficacy of carbon sequestration and effectiveness, but also with respect to the timeframe to subsequent  $N_2O$  emission. At present, the majority of  $N_2O$  turnover occurs in the upper 300 m (Codispoti et al. 2001) and so ventilation to the atmosphere will be within a 100 yr timeframe.

### LONGER-TERM EFFECTS ON $N_2O$

Extrapolations and models provide some insight into the longer-term effects of OIF that defy observational capability. For example, remineralization of the additional carbon fixed during SOIREE was estimated to subsequently produce 2.1 to 4.1 t of  $N_2O$  (Law & Ling 2001), assuming Redfield stoichiometry and a nitrification: $N_2O$  production rate of 0.25 to 0.5 % (Goreau et al. 1980). Due to the high GWP of  $N_2O$ , this would offset the reduction in radiative forcing achieved through increased carbon fixation by at least 6 to 12 % (Law & Ling 2001). Initial model estimates of long-term (100 yr) iron fertilization of the Southern Ocean, based on the assumption of complete macronutrient drawdown, suggested that increases in  $N_2O$  production could completely offset the benefit gained by increased carbon

fixation (Fuhrman & Capone 1991, Law & Ling 2001). More recent analysis of Southern Ocean iron fertilization using 3D models suggests a more conservative offset of 6 to 18 % due to downstream far-field effects, as iron-stimulated macronutrient utilization increases local  $N_2O$  production, but reduces production in the tropics due to decreased macronutrient supply (Jin & Gruber 2003). However, Jin & Gruber (2003) identify a more significant  $N_2O$  offset of 37 to 47 % from fertilization of the tropics, increasing to 58 to 194 % when fertilization was limited to 10 yr. The latter arises from the disproportionate effect of long-term decreases in dissolved oxygen and associated  $N_2O$  production relative to a shorter period of  $CO_2$  drawdown. These examples illustrate the necessity to consider long-term  $N_2O$  production when determining potential sites and duration of OIF. In particular, for assessment of any future OIF should address the model predictions that (1) small-scale and/or shorter-term fertilization may not reduce  $N_2O$  production and emissions proportionally, (2) cessation of fertilization will not bring  $N_2O$  production back to baseline levels in the short-term, and (3)  $N_2O$  production hotspots may relocate (Jin & Gruber 2003).

Monitoring of potential adverse effects is a key issue for future OIF, as identified by the recent London Convention (2007) statement, which recommended evaluation of 'potential impacts of gases that may be produced by the expected phytoplankton blooms or by bacteria decomposing the dead phytoplankton' (London Convention 2007, p. 2). This presents a challenge for  $N_2O$ , as any perturbation will be small relative to a background signal that exhibits natural spatial variability; for example,  $N_2O$  at 200 m to 800 m may exceed 1000 % saturation in upwelling regions (Law & Owens 1990). In addition,  $N_2O$  will be responsive to climate change as warming of the ocean will decrease oxygen solubility and increase bacterial remineralization (Schmittner et al. 2008), thus complicating attribution of increases in  $N_2O$  to OIF. Current technology limits the capacity for monitoring, as autonomous *in situ*  $N_2O$  sensors are insufficiently sensitive to measure  $N_2O$  concentrations (5 to 30  $nmol\ l^{-1}$ ) in the open ocean. Shipboard techniques using electron capture detector gas chromatograph (ECD-GC) provide sufficient sensitivity but limited vertical resolution and areal coverage; they are sufficient for surface mapping of  $N_2O$  distribution, but not for following mid-water  $N_2O$  production and along-isopycnal transport over distances of 1000s of km. An alternative approach for monitoring over large spatial and temporal scales is to use  $O_2$  concentration as a proxy for  $N_2O$ , by utilizing the parameterization for  $N_2O$  as a nonlinear function of  $O_2$  and depth (Nevison et al. 2003).  $O_2$  optode measurements on Argo floats show considerable promise

for broad-scale mapping of oxygen in intermediate and deep waters (Roemmich et al. 2004, Riser & Johnson 2008), and provision of a large pre-fertilization database against which post-OIF changes in oxygen and  $N_2O$  could be assessed. This approach could be augmented using oxygen optodes on gliders for repeat transect measurements and by the use of passive and deliberate tracer distributions on isopycnals for attribution of changes in oxygen and  $N_2O$  to OIF. Use of dissolved  $O_2$  as a proxy would require further validation of the  $N_2O$ – $O_2$  relationship and its regional variability. For example, variability may arise from changes in iron availability; iron is a component of ammonium monooxygenase and hydroxylamine oxidase enzymes (Moir et al. 1996, Zahn et al. 1996) and so may influence both nitrification rate and  $N_2O$  yield. In addition,  $N_2O$  yield may be influenced by nitrogen fixation (Nevison et al. 2003), which warrants further investigation as iron availability is a limiting factor for nitrogen fixation in low latitude waters (Mills et al. 2004).

#### DMS AND OIF

DMS represents a potential link between the iron and Charlson-Lovelock-Andreae-Warren (CLAW) hypotheses (Charlson et al. 1987, Martin 1990), which have together dominated surface ocean biogeochemical research over the last decade. DMS has a short atmospheric lifetime and may influence climate change via particle formation and alteration of atmospheric albedo. The CLAW hypothesis (Charlson et al. 1987), which invokes oceanic regulation of climate via phytoplankton production of DMS precursors, DMS emission, and aerosol and cloud condensation nuclei (CCN) production that influences atmospheric albedo, still remains to be proven some 20 yr after inception (Harvey 2007). This reflects both its inherent complexity and the logistical difficulty of relating a variety of biogeochemical, physical and photochemical processes occurring at different spatial and temporal scales, as recently summarized in a series of papers in *Environmental Chemistry* (2007, Vol. 4). Nevertheless, as the DMS precursor dimethylsulphonopropionate (DMSP) is produced by certain phytoplankton groups and initial paleoceanographic evidence indicated a sulphur–iron–climate link (Legrand et al. 1988), the potential for iron-mediated DMS production has been well studied, with DMS measurements on 9 of the 12 FeAXs (Boyd et al. 2007). Initial confirmation was provided by the first 4 FeAXs in the equatorial Pacific and Southern Oceans, which exhibited similar trends of increased production of DMSP followed by DMS increases (1.5- to 6.5-fold) associated with a decline in nanophytoplankton (2 to 20  $\mu m$ ) stocks 12 to 14 d after

fertilization (Turner et al. 2004). Consistent with this, a 5-fold increase in DMS was observed during the subsequent Southern Ocean Iron Experiment (SOFEX) campaign and extrapolated regionally to suggest that iron fertilization of the Southern Ocean could potentially double global DMS emissions ( $14 \text{ Tg S yr}^{-1}$ , Wingenter et al. 2004). A subsequent more conservative estimate, based upon iron fertilization of 2% of the Southern Ocean, suggested a 20% DMS increase that could produce a  $2^\circ\text{C}$  decrease over the Southern Ocean via the CLAW hypothesis (Wingenter et al. 2007).

However, subsequent FeAXs in the north Pacific exhibited significant departures from the initial experiments (Fig. 1), with no significant change in DMS during SEEDS (Sub-Arctic Pacific Experiment for Ecosystem Dynamics Study) despite the highest response in chlorophyll concentration observed in a FeAX (Takeda & Tsuda 2005, Boyd et al. 2007). Furthermore, in the most detailed FeAX study of DMS cycling during SERIES, the initial increase in nanophytoplankton stocks and DMSP was instead followed by only a minor increase in DMS, with a subsequent decline to concentrations one order of magnitude lower than surrounding unfertilized waters (Levasseur et al. 2006, Merzouk et al. 2006). Instead of DMS production initiated by herbivory, as in previous FeAXs, increases in bacterial production and associated sulphur demand resulted in DMSP and DMS utilization. This variability in DMS response to iron addition, with Southern Ocean waters representing a significant DMS source and the sub-arctic Pacific a sink, indicates the need for comparative studies to determine the origin of regional variation. It is also a good illustration of the importance of extrapolating individual FeAX results on a regional basis, rather than to the global ocean. Recent palaeorecord analysis found no co-variation of non-sea salt sulphate, a DMS proxy, with glacial–interglacial variations in dust supply (Wolff et al. 2006). As the role of iron as a major control of DMS has become less certain, other factors such as UV-radiation have been identified as important drivers of DMS seasonality (Vallina & Simo 2007). Indeed, the potential myriad responses of DMS to the interaction of climate-reactive physical and biogeochemical drivers (Harvey 2007) presents large uncertainty in the prediction of future DMS emissions, even without the confounding influence of OIF.

Monitoring of DMS in the ocean is currently limited to shipboard measurement as autonomous sensors of sufficient sensitivity are not available. However, recent analytical advances include the Membrane Inlet Mass Spectrometer, which has the capacity for sampling dissolved DMS at high spatial resolution (Tortell 2005), and the Atmospheric Pressure Ionization Mass Spectrometer (APIMS), which provides direct measurement

of atmospheric DMS (Huebert et al. 2004) on both research vessels and aircraft. Verification and attribution of changes in aerosol concentrations and CCN arising from iron-induced DMS production is more challenging. Atmospheric sulphur measurements during SERIES attempted to characterize downwind aerosol composition, but were complicated by the size of the patch relative to the large wind fetch (Phinney et al. 2007). This reflects the difficulty of positioning and scaling shipboard air measurements relative to a small-scale (100 to 500 km<sup>2</sup>) patch, and thus the requirement for rapid and adaptive airborne measurements on timescales of <24 h. Characterization of seasonal and regional variability in marine DMS and atmospheric sulphur and aerosol composition (Boers et al. 1998) should be a pre-requisite of future OIF. 'Natural laboratories,' such as phytoplankton blooms at open-ocean frontal regions and island wakes, offer potential for studying both DMS cycling and associated aerosol production prior to OIF. Such natural laboratories would be ideally sited in the southern hemisphere, due to the favourably low background aerosol concentration at accessible locations for repeat aircraft sampling.

#### NET IMPACT OF OIF ON ATMOSPHERIC PROCESSES

DMS and N<sub>2</sub>O have been used above to illustrate the issues relating to prediction and monitoring of trace gas response to OIF. Other trace gases monitored during FeAXs include carbon monoxide and methane, which decreased and increased, respectively, during SOFeX, and isoprene, which increased 5- to 6-fold during SOFeX and SERIES (Fig. 1) (Wingenter et al. 2004, Moore & Wang 2006). These trace gases react with hydroxyl radicals in the troposphere, so variation in their marine emission will influence the atmospheric lifetime of other short-lived OH-reactive gases, such as DMS and halocarbons. Consequently, altered emissions of different trace gases could have positive or negative synergistic effects on atmospheric processes. Halocarbons have also exhibited a range of responses in FeAXs (Fig. 1), with positive, negative and negligible responses observed in methyl bromide and methyl iodide concentrations (Wingenter et al. 2004, Liss et al. 2005, Moore & Wang 2006), potentially reflecting regional variations in photochemistry and plankton community composition. Secondary effects on atmospheric chemistry and climate may also arise from OIF via changes in halocarbon emissions, for example, with increased methyl bromide emissions in the Southern Ocean potentially delaying the recovery of stratospheric ozone (Wingenter et al. 2004). For comprehen-

sive monitoring and modeling of OIF, it is then essential to determine the net effect of changes in emissions of different trace gases on atmospheric processes and climatic forcing, with priority on the radiative balance and tropospheric oxidation capacity. This information should then be summarized in a similar manner to the IPCC radiative forcing components (IPCC 2007), an approach that would facilitate assessment of both iron-mediated changes on individual trace gases and the net impact on climate and atmospheric composition, and so assist monitoring bodies and policy makers in determining the impacts of ocean iron fertilization.

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