Carbon Sequestration Through Oceanic Fe Fertilization: Opportunity for Mine Water?

Benjamin C. Hedin, Robert S. Hedin

Hedin Environmental, 195 Castle Shannon Blvd., Pittsburgh, Pennsylvania, USA, ben.hedin@hedinenv.com

Abstract John Martin first proposed the iron hypothesis in 1990 which suggests that ocean iron concentrations impact phytoplankton growth which impact global climate. Subsequent experiments have confirmed this hypothesis and demonstrated unique ocean conditions that are suited for sequestering atmospheric carbon and increasing the productivity of local food chains. In this paper, we review the literature of ocean iron fertilization experiments and perform calculations to evaluate the opportunity for using mine drainage by-products in future geoengineering proposals.

Keywords IMWA 2013, iron fertilization, carbon sequestration, mine water

Introduction

Large portions of oceans have low productivity despite available nutrients. These areas, called high nutrient low chlorophyll (HNLC), characteristically have an abundance of macronutrients, such as nitrate and phosphorous, yet phytoplankton populations are relatively small and rarely bloom. These conditions persist because of iron limitations. John Martin first made the connection between chronically low iron concentrations and low productivity in 1990 when he proposed the iron hypothesis which states that ocean iron concentrations impact phytoplankton populations which affect global climate (Martin 1990). Specifically, that during the last glacial maxima, aerosol iron concentrations were 50 times higher than the last interglacial period. This increase in iron likely affected atmospheric CO_2 concentration quickly, in just a few hundred years. The specific mechanism of the carbon sequestration was the sinking of phytoplankton to ocean sediments.

Martin also acknowledged the possibility of iron fertilization as a geoengineering option to sequester CO_2 from the atmosphere into ocean sediments. Recent CO_2 sequestration interests have raised the profile of ocean iron fertilization (OIF) projects. Because mine water professionals commonly deal with large excesses of iron, the purpose of this paper is to review the best iron fertilization information currently available and provide calculations that assess the opportunity for mine water or mine water solids to increase CO_2 sequestration and the productivity of ocean ecosystems.

Background

The major natural source of iron to pelagic environments is wind-blown dust. Iron is used by phytoplankton, cyanobacteria and bacteria for fixing atmospheric nitrogen, reducing nitrate and chlorophyll synthesis (Martin 1990). Lab experiments have shown that very little iron is needed for substantial phytoplankton growth and C:Fe molar ratios ranging from 140,000 to 500,000 have been reported (Buesseler & Boyd 2003). Where iron is limiting, such as HNLC waters, the addition of iron can have a huge impact on primary productivity.

To date, thirteen OIF experiments have been conducted around the globe in various ocean conditions. Between 350 and 10,000 kg of iron sulfate dissolved in acidified sea water have been discharged into the ocean in pulsed doses, similar to episodic dust events. Although fertilization typically increases local Fe concentrations by less than 1 mmol/m^2 and raises Fe concentrations to no more than 10 µg/L Fe, the result is phytoplankton blooms that persist for weeks. Monitoring vessels have collected data on blooms for only a few days to over a month. Unfortunately no vessel has monitored a bloom's complete development and collapse. Often, OIF experiments are carried out in eddies because they can be identified by satellites and the waters inside and outside an eddy, to a large extent, do not mix, allowing for comparison between fertilized and unfertilized conditions over a small area. During a bloom many variables are monitored to allow for the calculation of chlorophyll concentration, nutrient concentrations (nitrate, dissolved inorganic carbon, particulate organic carbon and silicon), particulate organic carbon concentration and dominant phytoplankton as well as zooplankton, among others (Boyd *et al.* 2007).

OIF experiments have demonstrated that iron fertilization increases productivity, decreases dissolved inorganic carbon and decreases nutrients. The composition of the plankton blooms has varied. Of eleven OIF experiments that produced a bloom, diatoms emerged as the dominant organism in seven. Diatoms are phytoplankton encased in silica which not only allows them to avoid predation, but causes them to sink after death, exporting particulate organic carbon to the ocean floor where it is considered isolated for centuries (Boyd *et al.* 2007; Coale *et al.* 2004).

Carbon Sequestration Potential

About 20 % of the worlds' oceans are characterized as HNLC areas. A major HNLC area is the Southern Ocean which is generally defined to be south of 60° latitude, with an area of approximately 20 Mkm^2 (Fig. 1). In this area, a large amount of unused surface macronutrients are returned to the deep ocean. Four OIF experiments have been performed in the Southern Ocean, all resulting in phytoplankton blooms, confirming that iron limits primary production (Buesseler & Boyd 2003; Smetacek *et al.* 2012).

The most detailed OIF experiment in the Southern Ocean was the 2004 European Iron Fertilization Experiment (EIFEX). The experiment consisted of two fertilizations of 7 t of iron sulfate each, separated by 14 days. Over the 37 day experiment, water chemistry was measured over a vertical depth gradient of up to 3,000 m. Surface concentrations of nitrate, nitrite and dissolved inorganic carbon decreased inside the fertilized patch yet remained stable outside the patch. Additionally, surface concentrations of chlorophyll, particulate organic carbon, particulate organic nitro-

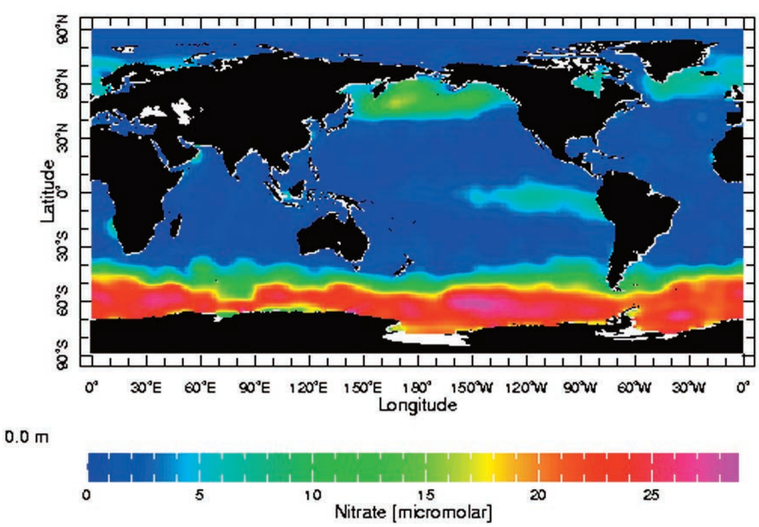

Fig. 1 *Areas of the ocean with abundant nitrate are deemed HNLC areas. Data from www.geos.ed.ac.uk/homes/s0675905/MScBSc.html*

gen and biogenic silica all increased inside the fertilized patch yet remained stable outside (Fig. 2). All of these variables indicate a Fe-induced phytoplankton bloom, of which 97 % was due to large diatom proliferation because of available silica (Smetacek *et al.* 2012).

The research team recorded particulate organic carbon concentrations throughout the depth gradient as an indicator of sinking and possibly sequestered of carbon. Around 24 days after initial fertilization, particulate organic carbon stocks increased sharply below 200 meters depth as diatoms died en masse and formed sinking aggregates. Increases in particulate organic carbon from 300 to 3,000 m were accompanied by decreases near the surface (Smetacek *et al.* 2012).

The authors calculated an iron induced increase in C fixation by phytoplankton of 2.4 mol/m², of which 1.2 mol/m² sank below 1,000 m. The resulting C:Fe molar ratio of iron induced carbon export was 6,667. The authors consider these measurements underestimates because the bloom had not yet reached an iron limiting state, enhanced primary production and carbon flux continued after monitoring had ended and chlorophyll concentrations inside the patch were still above pre fertilization and outside-patch concentrations (Smetacek *et al.* 2012).

Increasing Productivity

Iron fertilization of silica deficient water also induces large phytoplankton blooms, but diatoms are a small percentage. To investigate the role of silicon in the iron hypothesis, simultaneous OIF experiments in silicon rich and deficient portions of the Southern Ocean were conducted in 2002. Although both fertilization events resulted in phytoplankton blooms, diatoms made up less than half of the low silicon bloom and most of the high silicon bloom. The maximum primary productivity rate in the silicon deficient bloom was double that of the silicon rich bloom. Although limited carbon was exported to the ocean floor due to lack of diatoms in the silicon deficient bloom, proliferation of other phytoplankton could have impacts several levels up the trophic chain (Coale *et al.* 2004).

Among the ten OIF’s that measured an increase in chlorophyll, half recorded an increase in zooplankton stocks suggesting that increasing oceanic primary productivity could affect the local food chain (Boyd *et al.* 2007). Such is illustrated in a recent 2009 OIF experiment in a silicon deficient portion of the south-western Atlantic. A short initial non-diatom phytoplankton bloom produced a zooplankton bloom that kept the phytoplankton population in check (Mazzocchi 2009).

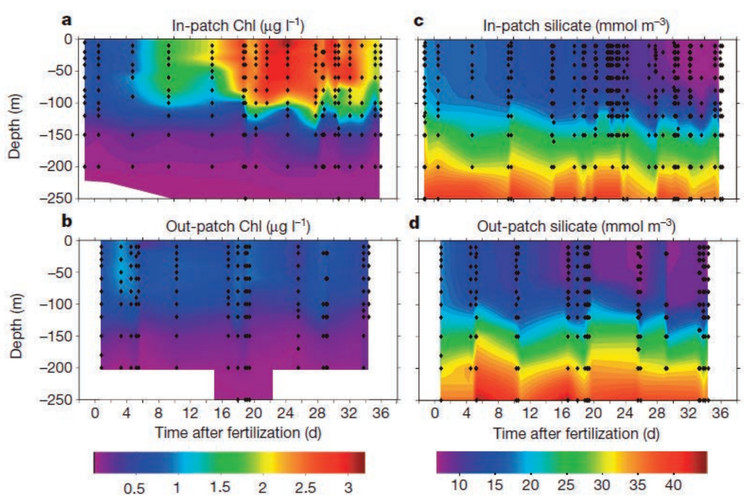

***Fig. 2** High chlorophyll concentrations inside the fertilized patch (a) and low outside of the patch (b). Silicate concentrations decreased inside the fertilized patch (c) but stayed stable outside (d) Smetacek et al. 2012.*

Geoengineering

The results of all OIF experiments to date indicate that iron fertilization initiates a phytoplankton bloom that could sequester carbon as well as enhance the entire local food chain. As mentioned before, certain areas of the ocean are conducive for each respective task. Here, we will present rough calculations that explore sequestering carbon and increasing productivity on a large scale.

Accepting the iron hypothesis, geoengineering of our current climate by sequestering carbon into ocean sediment is possible. Based on the 2004 EIFEX data, the authors calculated the sequestration of 1.2 mol C/m^2 from a single iron fertilization event. Extrapolating this result to half of the Southern Ocean (10.15 Mkm^2) suggests that 161 Mt of carbon could be sequestered through the application of 113,000 t of Fe. During the course of the EIFEX bloom, silic acid concentrations halved and nitrate + nitrite concentrations only slightly decreased. Therefore, assuming silicon is the limiting nutrient in diatom blooms, sequestered carbon could double to 323 Mt. Although the complete collapse of the diatom bloom was not observed during the 37 day EIFEX experiment, a decline was evident from decreases in surface particulate organic carbon stocks and increases of deep particulate organic carbon stocks late in the experiment. Assuming the bloom was close to collapsing, iron fertilization could take place every 4 months to allow HNLC conditions to be reestablished. Thus, a regular OIF regime in 50 % of the Southern Ocean could sequester 1.29 Gt of carbon per year (table 1). For context, the total C emissions of the world's cement industry are about 1 Gt of carbon per year.

A consistent and large scale OIF, such as the one mentioned above, would require 901 kt of iron per year based on a C sequestered: Fe added weight ratio of 1,434. This is a huge amount of Fe. Estimates of the amount of Fe produced annual by mine water systems worldwide are unknown to the authors, but are suspected to be much less than this quantity. The authors are familiar with iron production by mine water systems in the coalfields of the eastern US. The largest iron-producing passive system in the eastern U.S. creates 292 t/a Fe (Hedin 2006). The authors estimate that in southwestern Pennsylvania, the annual iron discharge from flooded coal mines is approximately 10,000 t/a Fe (100,000 gpm [6.31 m^3/s] at 50 mg/L Fe). While this iron loading is only a fraction of the total shown in Table 1, it is enough to theoretically sequester 14 Mt of carbon.

The value of large ocean iron fertilization efforts depends on the value of sequestered carbon and the value of increased ocean productivity. The value of carbon sequestration can be estimated from carbon credit markets. Although, the carbon market is quite unstable at this time, carbon credits currently sell for approximately $10/t C in California, $4/t C in Europe and $0.14/t C in New Zealand. Based on these prices, and the sequestration scenario shown in Table 1, the gross value yielded from

	Value	Source
Iron induced carbon sequestration	14.4 g C/m^2	Smetacek *et al.* 2012
Area of Southern Ocean	20.3 Mkm^2	www.worldatlas.com
Carbon sequestration with fertilization of half of Southern Ocean (one event)	161 Mt C	Calculation
All available silicon used for diatom growth (one event)	323 Mt C	Assumption
Sequestration at 4 events per year	1.3 Gt C	Assumption
C sequestration: Fe fertilization, mass ratio	1,434	Smetacek *et al.* 2012
Fe fertilization requirement per year	901 kt Fe	Calculation

Table 1 *Carbon sequestration potential of the Southern Ocean.*

a ton of iron used in ocean fertilization ranges between $430/t (New Zealand) and $14,340/t (California).

Although fertilization of ocean waters low in silica does not sequester much carbon, the increase in primary productivity could be useful for stimulating the local food chain. Authors of the 2004 EIFEX study calculated that one ton of iron stimulated 2,868 t of carbon uptake. Based on previously mentioned OIF experiments, high temperature and low silicon concentrations can double primary productivity rates in the Southern Ocean and promote non-diatom phytoplankton growth (Coale *et al.* 2004). A doubling of primary production results in a carbon to iron ratio of 5,735. Proliferation of non-diatom phytoplankton leads to increases in zoo plankton populations and, presumably, higher trophic level organisms. Although no scientific experiments have examined OIF potential in this regard, a recent unscientific OIF off of British Columbia, Canada, attempted to increase productivity of the local salmon fishery. Table 2 shows calculations for the impact of an OIF where the target is predatory fish atop a five trophic level food chain that has 10 % C transfer between trophic levels. The calculations suggest that one pound of iron could result in 0.57 lb (0.3 kg) of predatory fish. The wholesale price for salmon in California in 2012 was $4-6/lb. One ton of iron fertilization theoretically yields 0.57 t salmon which has wholesale value of $4,560 – $6,840.

The cost of supplying iron for OIF's depends on the source of iron. Iron oxide produced from coal mine drainage in Pennsylvania currently sells for $575 per ton Fe. High purity synthetic iron oxide sells for $1,150/t Fe. Iron sulfate heptahydrate, the product used in most OIF experiments sells for $500/t Fe.

Trophic Level	C:Fe ratio
1 (Primary Producer)	5,735
2 (Zooplankton)	573.5
3 (Predatory Zooplankton)	57.35
4 (Grazers)	5.74
5 (Predatory Fish)	0.57

Table 2 *Tentative calculations of impact of OIF on local trophic chains.*

Conclusion

OIF experiments confirm Martin's iron hypothesis that adding iron to ocean environments will increase primary productivity. However, specific ocean chemistry is required to sequester carbon or increase food chain productivity. HNLC areas, specifically those high in silicon, such as the Southern Ocean, are required to promote diatom blooms that can sequester atmospheric carbon in ocean sediments. Fertilization of low silicon, warm ocean waters can promote a non-diatom phytoplankton bloom with possible impacts to the local food chain.

The potential for stimulation of the ocean's productivity with iron is huge. A concerted effort to increase the productivity of the Southern Ocean could consume 900 kt of iron annually. The amount of iron produced by active and closed mining operations is unknown, but it appears to be much less than this quantity.

The value of large scale OIF was estimated from the results of EIFEX and the current market value for carbon credits and salmon. The highly volatile carbon credit market yields values of $430 – $14,340 per ton Fe. Stimulation of a salmon fishery, assuming that the increased fish can be captured, yields a value of $4,560 – $6,840 per ton Fe. The current cost to produce an iron oxide product from mine drainage is $575/t Fe, while the cost for iron sulfate is $500/t Fe.

References

Boyd PW, Jickells T, Law CS, Blain S, Boyle EA, Buesseler KO, Coale KH, Cullen JJ, de Baar HJW, Follows M, Harvey M, Lancelot C, Levasseur M, Owens NPJ, Pollard R, Rivkin RB, Sarmiento J, Schoemann V, Smetacek V, Takeda S, Turner S, Watson AJ. (2007) Mesoscale Iron Enrichment Experiments 1993-2005: Synthesis and Future Directions. Science 315:612-617.

Buesseler KO, Boyd PW (2003) Will Ocean Fertilization Work? Science 300:67-68.

Coale KH, Johnson KS, Chavez FP, Buesseler KO, Barber RT, Brzezinski MA, Cochlan WP, Millero FJ, Falkowski PG, Bauer JE, Wanninkof RH, Kudela RM, Altabet MA, Hales BE, Takahashi T, Landry MR, Bidigare RR, Wang X, Chanse Z, Strutton PG, Friederich GE, Gorbunov MY, Lance VP, Hilting AK, Hiscock MR, Demarest M, Hiscock WT, Sullivan KF, Tanner SJ, Gordon RM, Hunter CN, Elrod VA, Fitzwater SE, Jones JL, Tozzi S, Koblizek M, Roberts AE, Herndon J, Brewster J, Ladizinsky N, Smith G, Cooper D, Timothy D, Brown SL, Selph KE, Sheridan CC, Twining BS, Johnson ZI. (2004) Southern Ocean Iron Enrichment Experiment: Carbon Cycling in High- and Low-Si Waters. Science 304:408-414.

Hedin RS (2008) Iron removal by a passive system treating alkaline coal mine drainage. Mine Water Env. 27:200-209

Martin JH (1990) Glacial-Interchange CO2 Change: The Iron Hypothesis. Paleoceanography 5(1):1-13.

Mazzocchi MG, González HE, Vandromme P, Borrione I, d'Alcalá MR, Gauns M, Assmy P, Fuchs B, Klaas C, Martin P, Montresor M, Ramaiah N, Naqvi W, Smetacek V. (2009, October) A non-diatom plankton bloom controlled by copepod grazing and amphipod predation: Preliminary results from the LOHAFEX iron-fertilisation experiment. GLOBEC International Newsletter 15(3):3-6.

Smetacek V, Klaas C, Strass VH, Assmy P, Montresor M, Cisewski B, Savoye N, Webb A, d'Ovidio F, Arrieta JM, Bathmann U, Bellerby R, Berg GM, Croot P, Gonzalez S, Henjes J, Herndl GJ, Hoffman LJ, Leach H, Losch M, Mills MM, Neill C, Peeken I, Röttgers R, Sachs O, Sauter E, Schmidt MM, Schwarz J, Terbrüggen A, Wolf-Gladrow D. (2012) Deep carbon export from and Southern Ocean iron-fertilized diatom bloom. Nature 487:313-319.