



A nature-based negative emissions technology able to remove atmospheric methane and other greenhouse gases

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ABSTRACT

Fulfilling the Paris Climate Agreement requires reducing rapidly the new emissions of greenhouse gases (GHGs) to reach net zero by 2050. As some anthropogenic emissions cannot be zero, to compensate them it will be necessary to remove GHGs from the atmosphere. Among possible methods, the Iron Salt Aerosol (ISA) offers new possibilities, including removal of methane and several other GHGs, as well as carbon dioxide. Several studies suggest that anthropogenic emissions of iron participate in the current primary productivity. As plans to decarbonize the world economy might also have inadvertent warming effects due to the reduction of iron emissions from fossil fuels burning, iron additions might help address this issue. ISA is different from the method known as Ocean Iron Fertilization and the differences are explained. ISA mimic natural processes and the dust which probably participated in the cooling during the ice-ages over the past million years. Still larger laboratory trials, safety and environmental impact studies and global chemical computer modeling are necessary before ISA would be ready to be trialed. Desk and laboratory studies indicate low cost, easy deployment and efficacy, all of which can be validated by future small scale field trials, a step needed before, if successful, a possible implementation at a climate-relevant scale.

1. Introduction

The Paris climate agreement called to limit global warming to less than 2 °C above pre-industrial levels, and is the biggest challenge humanity must meet (Anderson 2016). IPCC Integrated Assessment Models and scenarios show that limiting warming must combine reduction of GHG emissions with removal of GHGs from the atmosphere (Anderson 2016) through deployment of Negative Emissions Technologies (NETs).

Numerous NETs have been proposed, with the majority focusing on carbon dioxide removal (de Richter et al., 2018; McLaren 2012). But non-CO₂ GHGs, predominantly methane, provide nearly 35% of the climate forcing (Blasing 2016) by well-mixed GHGs. The global warming potential of CH₄ ranges from about twenty eight to eighty four times

more than CO₂ on 100 year and 20 year timescales respectively (Myhre et al., 2013), therefore making CH₄ removal important for overall work to address climate change. The Iron Salt Aerosol (ISA) technology described in this article can oxidize CH₄ into CO₂, while also causing other cooling effects (Oeste et al., 2017).

Anthropogenic sources now add about forty billion tons of carbon dioxide and CO₂ equivalent (CO₂-eq) to the atmosphere every year (CA&NCI 2019). More than a trillion tons of CO₂-eq would need to be removed (Allen et al., 2009) to restore the CO₂ level of the early Holocene (280 ppm) (Harvey et al., 2013; Indermühle et al., 1999). To remove billions of tons of CO₂ per year (Herzog 2011), other proposed NETs generally require huge new infrastructures. The next section explains how the Iron Salt Aerosol (ISA) nature-based method for

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Greenhouse Gases Removal (GGR), if its safety is proved, could be a simple, safe and quite cheap way to remove some warming compounds including CH₄, CO₂, some tropospheric O₃, some black carbon (BC) (Raju et al., 2020), by replicating the iron-rich dust production that might have helped to cool the planet in Ice Ages (Abadi et al., 2020; Sur et al., 2015).

Reducing emissions to net zero by mid-century, while maintaining energy use, would require zero-carbon energy sources, with remaining emissions balanced by NETs. But even ending all CO₂ emissions would not be nearly enough to prevent dangerous warming (EASAC 2018), due to the committed warming effects of CO₂ from previous emissions. Feedback amplification of warming from past emissions is already underway, leading to possible tipping points (Lenton et al., 2019). As well, ending CO₂ emissions would not reduce all the emissions of other GHGs in particular from the agricultural sector, nor the GHGs already in the atmosphere. Significant reductions of the emissions of anthropogenic GHGs, as well as large scale removal of the existing atmospheric stock of GHGs are the principal options to prevent and reverse dangerous global warming (Pires 2019; Realmonte et al., 2019).

Extensive scientific and policy-oriented discussion of ISA has occurred since 2017 (Oeste et al., 2017), notably the recognition that the atmospheric methane removal potential of ISA may justify the interest of the scientific community and more deep research in this field, before testing in field conditions. This new review completes the previous one (Oeste et al., 2017), by clarifying many aspects, simplifying and explaining the difference between Ocean Iron Fertilization (OIF) and ISA, as well as by providing new information on recently elucidated possible carbon storage mechanisms in the ocean.

A short overview of some of the fertilizing effects of iron compounds over the continents and the oceans is given in the next section as well as an explanation of the differences between OIF and ISA. Section 3 describes the expected tropospheric effects of ISA on several GHGs such as CH₄ and O₃, section 4 explains more deeply the possible global deployment of ISA, the discussion in section 5 addresses safety and health aspects, as well as the research still needed before field trails, followed by concluding remarks on section 6.

2. Cooling and fertilizing effects of existing iron emissions

Iron is a decisive factor in natural processes that regulate primary productivity, and several atmospheric GHGs. This section outlines some primary effects of iron on atmospheric, marine and land chemistry.

2.1. Biological need for iron

Iron is an essential micronutrient for many physiological processes and bio-functions. Plants need iron, for chlorophyll production, photosynthesis, nitrogen fixation and nitrate reduction, while animals need iron for oxygen transport and many enzyme functions. Human iron deficiency can cause anemia, heart failure, ulceration, skeletal weakness and cognitive disorders (Abbaspour et al., 2014; Aspuru et al., 2011).

2.2. Over the oceans

Ocean regions termed High-Nutrient–Low-Chlorophyll (HNLC), have low iron levels resulting in low plankton productivity. Phosphorus and nitrogen-rich but iron-poor, HNLC regions cover an estimated sixty million square kilometers, 20% of the ocean surface area, including parts of the equatorial and Northern Pacific and most of the Southern Ocean (Pitchford and Brindley 1999).

Iron is the 4th most abundant element in the earth's crust, but its solubility and bioavailability are low depending of its oxidation state and chemical form or environment. Consequently, large areas of the world's ocean are iron-deficient, as are calcareous alkaline soils where plants suffer from chlorosis as explained in the next subsection.

Primary productivity in HNLC oceanic regions is limited by the

availability of iron (Martin et al., 1994). Among other nutrients, desert and volcanic dust deposit iron in HNLC regions inducing algal blooms that can be detected by satellites. These blooms consume locally and momentarily large quantities of atmospheric CO₂, which might be released back in the atmosphere after microbial remineralization (Robinson et al., 2014), while some might be stored at the bottom of the ocean (Smetacek et al., 2012).

Mimicking natural iron deposition to HNLC regions by Ocean Iron Fertilization (OIF) or by ISA could increase productivity and might help decreasing the atmospheric CO₂ with a global cooling effect (Martin 1990).

2.3. Methods to increase iron level over the oceans: differences between OIF and ISA

Extensive research has been conducted into Ocean Iron Fertilization by ship-based addition of iron sulfate slurry (Güssow et al., 2010) but it has several limitations as a climate engineering scheme (Boyd and Bressac 2016; Chisholm et al., 2002; Johnson and Karl 2002). Environmental risks potentially associated with OIF include depletion of deep-water oxygen, increasing production of N₂O and CH₄, alteration of the food chain, promotion of toxic algae species, disruption of marine ecosystems and rapid organic carbon re-mineralization that causes CO₂ to resurface (Denman 2008). Therefore some researchers fear that the carbon consumed by phytoplankton blooms may return quickly to the atmosphere (Martin et al., 2013). Other experiments show that diatom blooms cause deep carbon export and storage (Smetacek et al., 2012) as explained in section 3.

OIF is different from Iron Salt Aerosol in many respects.

Iron Salt Aerosol would apply a concentration of iron to the ocean 2–3 orders of magnitude smaller than OIF, aiming to enhance marine phytoplankton growth, and induce other cooling effects in the atmosphere and over the continents (Oeste et al., 2017). The variety, scope and magnitude of the combined cooling benefits of ISA, notably its methane removal effect which is described in section 3, mean that most if not all criticisms of OIF do not apply to ISA. Testing ISA at small scale and extremely dilute levels might be a safe and effective way to inform the likely effects in field conditions.

Carbon export processes in the deep ocean are complex, time-varying and often decoupled from biological production (Boyd and Trull 2007), making the efficiency of carbon sequestration by OIF difficult to assess. Alongside the small size and number of OIF field tests, the difficulties of measurement explain why OIF experiments have shown widely varying export efficiency. Calculated C:Fe molar ratios (amount of carbon in biomass created to the amount of iron provided) in natural fertilization vary from about 2,400 to 800,000, with severe under-sampling allowing this wide range (de Baar et al., 2008). Studies of naturally iron-fertilized waters found carbon export efficiencies up to ten times (Blain et al., 2007) greater than short-term blooms induced by experimental ship-based addition of iron sulfate (De Baar et al., 2005). New OIF open field trials have been projected (Yoon et al., 2018), as well as new iron dust generation methods (Emerson 2019).

Past variability in the CH₄ and CO₂ atmospheric concentrations was synchronous with air temperature variations and dust deposition over Antarctica the last million years (Lamy et al., 2014; Martínez-García et al., 2011), leading to the theory that the iron content of dust fertilized the oceans and increased oceanic primary productivity, cooling the planet (Martin 1990). This hypothesis seems more and more consistent with new evidences while additional ones might help explaining the C-storage. Such as the hypothesis that the aluminum content of the dust might preserve biogenic matter from decomposition and decay, potentially enhancing the biological pump and allowing more carbon sequestration in the ocean depths (Zhou et al., 2018), or by an effect of particle ballasting (Heinemann et al., 2019), or by an amplification of the CO₂ downdrawn induced by iron fertilization and cooler temperatures due to air-sea disequilibrium (Khawiwala et al., 2019).

Iron also has other effects: in the oceans, nearly 90% of the CH₄ produced within the subsea floor is consumed by anaerobic oxidation by iron oxides and sulfate reduction (Sivan et al., 2016; Sivan et al., 2014). That means iron compounds in the oceans help to reduce the emissions of CH₄. This is also true in freshwater lake sediments (He et al., 2018; Thamdrup and Schubert 2013).

Among the anthropogenic sources of iron, a large fraction of pyrogenic iron emissions from biomass fires and fossil fuels burning is already in a soluble form, for instance as iron (II) sulfate (Ito et al., 2019; Rathod et al., 2020). Desert dust particles often contain poorly soluble iron oxides such as FeO, hematite Fe₂O₃ and magnetite Fe₃O₄ within aluminosilicates clays. Atmospheric aging in the troposphere, and in particular chemical and physical processing, by acidic processing, freezing and melting, plus hydration-dehydration cycles modify the hygroscopicity, together with light induced oxido-reduction processes (Struve et al., 2020), plus possible reaction with naturally occurring organic acids, result in formation of organic salts or complexes that increase the iron solubility by transforming iron oxides into iron oxyhydroxide FeO(OH) (ferrihydrite) (Shi et al., 2015).

As well as natural dust, iron is also present in the atmosphere due to industrial processes, mainly from coal and other fossil fuel combustion (Ito and Shi 2016) but also from the iron and steel industry (Guo et al., 2017; Jia et al., 2018). The steel industry is among the highest energy consumers (about 20% of total, mainly provided by coal) and polluters, being an important source (25–41 mg/m³ in some plants in China) of particulate matter emissions (Jia et al., 2018). In particular the sintering, the puddling and the steelmaking processes, emit the higher PM mass concentration, and then the rolling process, with iron (1–6 mg Fe/m³) and sulphates being the most important constituents, together with chlorine, titanium, calcium, aluminum and sodium (Guo et al., 2017; Jia et al., 2018).

The iron and steel industries were also among the highest industrial emitters of HCl, but nowadays with the flue gas desulfurization systems installed, the quantities have been significantly reduced (45–83%) in China (Ding et al., 2020). But, as the flue gas desulfurization systems don't remove them efficiently, it was found that high amounts (3.6 mg/m³) of short-lived chlorinated substances (CH₂Cl₂, CH₃Cl, C₂H₅Cl, and C₂H₄Cl₂) are emitted by the sintering processes, and those compounds are tropospheric sources of HCl (Ding et al., 2020).

These anthropogenic iron sources are much more soluble and bioavailable than natural ones (Ito and Shi 2016; Li et al., 2017; Rathod et al., 2020) because a large fraction of pyrogenic iron emissions from biomass fires and fossil fuels burning is already in a soluble form for instance as iron (II) sulfate (Hamilton et al., 2020; Ito et al., 2019; Rathod et al., 2020), while desert dust particles often contain poorly soluble iron oxides hematite Fe₂O₃ and magnetite Fe₃O₄ within aluminosilicates clays.

Over many oceanic regions, combustion processes are estimated to provide 20–100% of the soluble bio-available iron (Luo et al., 2008). According to Ito et al., (Ito et al., 2019; Ito and Shi 2016), this probably means that anthropogenic iron emissions from fossil fuel and other combustions processes or industries such as the iron and steel industries (Guo et al., 2017; Jia et al., 2018) might already play a major role in providing bio-available iron to some regions of the surface ocean (Sedwick et al., 2007), in particular in a significant portion of the Northern Hemisphere oceans (Ito et al., 2019; Ito and Shi 2016; Luo et al., 2008), and up to 68% over the Industrial Era (Hamilton et al., 2020). Some studies suggest that anthropogenic iron emissions could play a globally important role in marine productivity and carbon cycling (Pinedo-González et al., 2020) and might increase regionally the oceanic primary productivity (Ito et al., 2020; Liu et al., 2021). It has been suggested that this soluble iron might also deplete some other GHGs (Oeste et al., 2017), delivering several cooling effects (Oeste et al., 2017). If fossil fuel emissions are cut, these existing iron aerosols might need to be replaced to maintain the marine food web with the level of existing oceanic productivity, even if there is little C-storage, as

discussed in section 5.

2.4. Over the continents

The Amazon rainforest is fertilized by African dust, with iron and phosphorus carried across the Atlantic on the winds (Rizzolo et al., 2017; Yu et al., 2015).

For plants grown on alkaline soils (mainly calcareous) chlorosis induced by lack of iron is the main nutrient deficiency (Abadía et al., 2011; Basar et al., 2014; El-Jendoubi et al., 2014; Rombolà and Tagliavini 2006) potentially affecting some plants over more than 25% of the earth's land surface (Rombolà and Tagliavini 2006; Taalab et al., 2019). Consequently several methods of chlorosis correction are widely practiced in agriculture, such as iron foliar fertilization with iron sulfate and treatment of the soils with synthetic chelates of iron (Fernández et al., 2013). Oeste et al. (Oeste et al., 2017), reported that the deposition of desert dust containing iron, as well as the deposition of anthropogenic iron salt aerosols released by the steel industry and by burning coal might enable increased CO₂ uptake from terrestrial plants including trees and crops, as well as from phytoplankton and other marine plants.

This natural and anthropogenic iron deposition also appears to prevent to some extent some methane emissions. Experimental addition of humic acids and iron in wet sedge tundra landscapes significantly suppressed net methane fluxes (Miller et al., 2015), in Arctic peat ecosystems (Lipson et al., 2010) and in rice paddies (Ali et al., 2008; Liu et al., 2016; Liu et al., 2012; Wang et al., 2014). Addition of iron salts either inhibits methane emissions or enhances its oxidation rate (Rodén and Wetzel 1996). The anaerobic oxidation of CH₄ is important to limit its release into the atmosphere, with iron compounds playing a key role (He et al., 2018). Iron compounds also influence biomass humification rates (Zhang et al., 2017) and organic carbon preservation in soils (Lalonde et al., 2012).

3. Tropospheric impacts of iron

Atmospheric dust supplied high quantities of soluble iron to the ocean during glacial periods (Shoenfelt et al., 2018). This stimulated phytoplankton productivity (Shaffer and Lambert 2018) and might have contributed to drawdown of atmospheric CO₂ to levels of less than 200 ppm resulting in glaciations (Martin 1990; Martin et al., 1994; Martínez-García et al., 2009). Anthropogenic pollution emissions now contribute to enhance the natural bioavailability of iron in dust (Ito and Shi 2016; Li et al., 2017; Shi et al., 2009; Srinivas et al., 2014). The current iron level in the atmosphere is only about one third the estimated level at glacial maxima (Masson-Delmotte et al., 2010). 800,000 years of climate data from deep Antarctic ice cores reveal that during glacial and inter-glacial periods, the atmospheric concentration of CH₄ and CO₂ correlated with each other and also with dust levels (Köhler et al., 2010; Masson-Delmotte et al., 2010). The “iron hypothesis” (Martin 1990) was formulated in 1990, since then, 30 years later, the evidence accumulated convincingly shows that the Southern Ocean fertilization was indeed a leading actor in past glaciations (Stoll 2020). The suggestion that natural CO₂ atmospheric removal and cooling therefore appears to having possibly been caused by iron-rich dust increasing plankton productivity is supported by a range of theoretical connections between iron and carbon removal plus storage (Stoll 2020).

Why then did the CH₄ atmospheric concentration also decrease? In the troposphere, methane is currently mainly destroyed by the hydroxyl radical °OH, but atomic chlorine Cl• oxidizes about 1% (Wang et al., 2019) of the CH₄ (5.3 Tg/yr), or 3–4% according to older estimates (Allan et al., 2007). Atmospheric chlorine radicals are produced by several natural processes and also possibly by ISA (Thomas et al., 2006; Thornton et al., 2010). The Cl• creates a CH₄ sink that might have increased during glaciations (Levine et al., 2011), together with some other processes that reduced CH₄ production (Valdes et al., 2005).

There is no-known physical limitation to the FeCl₃ concentration in

the troposphere, specially under the marine boundary layer where sea-salt from sea-spray is abundant, as far as the acidity can be increased. After volcanic eruptions large emissions of mineral acids occur, among them hydrochloric acid, and molysite (FeCl_3) mineral deposits can be found in Italy, for instance near Naples from the Vesuvian, or near Pisa, close to the Amiata volcano in Tuscany. The chlorine chemistry has been proved in volcanic plumes (Baker et al., 2011). Some models estimate that over polluted coastal regions the methane removal might be up to 11.6% (Sommariva and von Glasow 2012), and no-known upper limit of methane removal by using Cl atoms has yet been determined.

The current status of atmospheric effects of ISA are mainly based on smog-chamber tests conducted at the University of Bayreuth, Germany in 2015–2017 which proved that ISA efficiently generates Cl atoms, and reacts with methane (Zetzsch et al., 2013) and other volatile organic compounds (VOCs). Tests now underway (2021) at the University of Copenhagen, Denmark aim to quantify these effects in a range of conditions and to determine the speciation of iron within the aerosols, and the number of CH_4 removed per atom of iron. In some smog-chamber tests, the efficiency of the chlorine catalysis was proven, with the generation of up to 78 chlorine atoms generated per hour per atom of iron (Wittmer and Zetzsch 2017). More research is needed regarding the atmospheric impacts, and the lifetime of the aerosols could only be determined during field tests which are still to be performed. Nevertheless, a global tropospheric chlorine chemistry model (Hossaini et al., 2016) evaluated the total amount of tropospheric Cl atoms and the amount of CH_4 eliminated by this sink: nearly 3.5 Cl atoms are needed for the removal of one CH_4 molecule as the Cl atoms (as well as the hydroxyl radicals $^{\circ}\text{OH}$) react faster with the other VOCs present than with methane. Wang et al. (Wang et al., 2019), estimated that globally in the troposphere the Cl atoms contribute to the oxidation of 20% of ethane, 14% of propane, but only to 1.0% of the oxidation of methane.

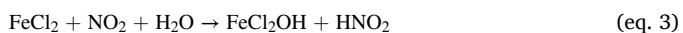
The Cl^{\bullet} are generated during the day by iron(III)/iron(II) photocatalysis (Wittmer et al., 2015a; Wittmer and Zetzsch 2017), according to the following reactions (list non-exhaustive):



Sunlight generates a free chlorine atom from iron trichloride



The chlorine radical breaks down methane



An atmospheric oxidant like NO_2 oxidizes iron(II) into iron(III)



Available acidity and chlorides from abundant sea-salt spray restores the iron trichloride.

The photolytic reaction of iron(III) chloride produces atomic chlorine and iron(II) chloride. The reaction of atomic chlorine by methane oxidation to hydrochloric acid and methyl radical is a first step of the total methane oxidation to CO_2 . The re-oxidation of iron(II) to iron(III) with an atmospheric oxidant such as NO_2 is a complicated chemical process, presented in a simplified way in equations (3) and (4) above (Finlayson-Pitts 1993, 2003).

These natural chemical reactions involve iron catalyzing the breakdown of methane by chlorine atoms, and show that artificially increasing the amount of iron salt aerosols in the troposphere might mitigate global warming in several ways (Oeste et al., 2017). The principal effects are by reducing the CH_4 concentration in the atmosphere, reducing plant chlorosis by deposition of iron on the continents, and inducing phytoplankton growth that enhances the oceanic food web (Oeste et al., 2017) and ocean productivity, after deposition of iron on the oceans. Together these and other ISA processes remove CO_2 and CH_4 from the atmosphere over both long term and short term.

Ozone (O_3) in the stratosphere forms the ozone layer that protects

the Earth from dangerous UV radiation. But O_3 in the troposphere is a major GHG and air pollutant, harmful to human and ecosystem health. Tropospheric O_3 destruction by reactive halogen species such as chlorine, bromine and iodine is well documented (Sherwen et al., 2016). During events of tropospheric O_3 depletion, over areas of several million km^2 , the surface ozone is completely destroyed in the lowest km of the atmosphere, producing a measurable cooling effect (Roscoe et al., 2001) and improved air quality (Muñiz-Unamunzaga et al., 2018). The photochemical activation of chlorine and bromine by iron salt aerosols (Wittmer et al., 2016; Wittmer et al., 2015b) is likely to enhance only marginally this process of surface O_3 removal, as ISA will not be deployed over urban areas, where pollution and combustions processes (transportation and domestic heating) are among the principal sources of tropospheric O_3 . No negative effect on stratospheric O_3 is anticipated, neither for the hydroxyl radical production, as the smog chamber tests proved that not only the generation of Cl atoms is enhanced, but also the hydroxyl radicals (Wittmer et al., 2015a; Wittmer and Zetzsch 2017), probably through Fenton and photo-Fenton reactions (Deguillaume et al., 2005; Nakatani et al., 2007).

The IPCC estimated in AR5 that tropospheric O_3 has provided 0.4 W per square meter of the increase in radiative forcing since 1750, nearly as much as methane. The ozone forcing is about 22% of the forcing from anthropogenic CO_2 (Myhre et al., 2013). But as stated above, mainly because of its targeted deployment zones far from urban polluted areas (see discussion on section 5), the effects of ISA are not expected to significantly affect global tropospheric ozone, neither the global oxidative capacity of the troposphere through the $^{\circ}\text{OH}$ radical generation, as the smog chamber tests proved an enhancement of the $^{\circ}\text{OH}$ generation (Wittmer et al., 2015a; Wittmer et al., 2015b; Wittmer and Zetzsch 2017), and as methane is the principal tropospheric sink of $^{\circ}\text{OH}$, and ISA might remove both methane and VOCs. Additional laboratory and field trials, as well as chemical modeling are still needed to measure the balance between the ISA effects on methane and VOCs removal, and the ozone and the $^{\circ}\text{OH}$ radical.

In the tropics, halogen chemistry is responsible for a large fraction (nearly 30%) of tropospheric O_3 destruction, but mainly due to bromine and iodine atoms (Read et al., 2008; Sommariva and von Glasow 2012). Globally, between 1 and up to 3–4% of CH_4 tropospheric destruction is due to chlorine (Lawler et al., 2009; Wang et al., 2019). In some coastal regions that experience polluted conditions the Cl^{\bullet} sink can account for >20% of boundary layer CH_4 oxidation (Hossaini et al., 2016), other models estimating the CH_4 destruction only up to 11.6% (Sommariva and von Glasow 2012).

The local albedo is increased by some types of aerosols which reflect sunlight radiation back to space, producing a cooling effect. Marine cloud brightening (MCB), produced by sea salt aerosol injection over the seas, has been suggested to enhance the cooling potential of low altitude clouds (Latham et al., 2012). A further climate outcome of iron addition to the oceans, possibly the greatest (Wingenter et al., 2007), is enhancing dimethyl sulfide (DMS) production by plankton causing regional cooling by increased albedo (Grandey and Wang 2015).

In summary, tropospheric iron aerosols (Ito and Shi 2016; Li et al., 2017) enable:

- (i) iron(III)/iron(II) photocatalysis under sunlight, generating chlorine atoms (Wittmer et al., 2016; Wittmer and Zetzsch 2016) which destroy CH_4 and some local surface O_3 ,
- (ii) deposition of soluble iron over iron-deficient oceanic regions enhances marine primary productivity (Maher et al., 2010; Okin et al., 2011),
- (iii) deposition of soluble iron over calcareous or alkaline soils enhances plant primary productivity (Abadía et al., 2011; Fernández et al., 2013; Rizzolo et al., 2017),
- (iv) cloud formation by DMS enhances the albedo (Wingenter et al., 2007).

All this indicates that current natural and anthropogenic emissions of iron salt aerosols might probably already cool the Earth by removing some CH₄, some O₃, and possibly CO₂ and other GHGs from the atmosphere, by enhancing albedo and by increasing oceanic and continental primary productivity (Ito and Shi 2015; Myriokefalitakis et al., 2015), and possibly also by inhibiting CH₄ emissions from soils (Hu et al., 2020; Jäckel and Schnell 2000).

4. The iron salt aerosol (ISA) method

The observations described in section 3 indicate that by increasing ISA production, several natural GHG removal mechanisms can be efficiently enhanced (Oeste et al., 2017). ISA differs from ship-based OIF methods in that its atmospheric cooling effects are likely to be more immediate and greater than its ocean fertilization cooling effect, enabling effective implementation with much lower concentrations of iron. However, as a nascent technology, modeling the chemistry of an ISA plume, as well as small scale scientific laboratory and field tests are needed to further quantify expected effects and demonstrate its safety and efficacy.

Oeste et al. (Oeste et al., 2017) found up to 12 cooling effects of iron derivatives in the oceans, in the troposphere and on land. For instance, iron derivatives might help reduce some amounts of airborne soot emitted by combustion processes (Rojas-Valencia et al., 2017) in case more iron fuel additives are used. Iron fuel additives containing potential ISA precursors such as iron picrate complex (Zhang et al., 2009) and ferrocene (Kasper et al., 1999) are commercially available to enhance combustion efficiency, reducing fuel consumption and soot emissions (Elwardany et al., 2020). Black Carbon (BC) or soot is not a GHG but it causes radiative forcing at a similar level to ozone and methane (Jacobson 2001; Myhre et al., 2013), consequently BC depletion or removal is useful. By darkening snow and ice surfaces, BC increases the melting of snow packs, sea ice and glaciers, and by forming heat

absorbing atmospheric brown clouds (Liu et al., 2019) it has a warming effect (Ramanathan and Carmichael 2008). The severe health effects of pollution are well known, with BC, Particulate Matter (PM) (Gustafsson and Ramanathan 2016) and surface O₃ (Anenberg et al., 2010) causing several million premature deaths annually worldwide, making reducing their levels highly beneficial for human health (Shindell et al., 2012). But ISA emissions and deployment as it is planned (see section 5) will have modest effects on surface O₃, BC and PM removal.

Rough estimation of the additional ISA quantities needed to slow-down global warming has been estimated (Oeste et al., 2017) at the equivalent of current anthropogenic ISA emissions by fossil fuel industries: 100,000 to 200,000 tons per year. Several ways to add the proposed quantity of iron in the lower troposphere are presented in Fig. 1 (Oeste et al., 2017), without the associated pollution of the current anthropogenic iron emissions.

The global jet fuel consumption is too low (about 240,000 t/yr) to help ISA deployment. Assuming a very high emission rate of 1 kg ISA iron precursor per ton of jet fuel, only 24 t/yr might be emitted. The global marine fuel consumption is estimated to about 450 million t/yr per year. If 300 ppm of iron could be added in the form of iron fuel additives to the fuel consumed by the shipping industry, then 135,000 tons of ISA could be produced. Meanwhile, for instance the German 3600 MW power station Niederaussem; which consumes 25 million t/yr of lignite (brown coal), can possibly emit 2831 t/yr of iron by burning 9438 t/yr of ferrocene. One hundred similar power plants can double the current anthropogenic emissions of iron (Oeste et al., 2017).

Those combustion processes don't directly emit FeCl₃, but FeO(OH) or Fe₂O₃, which, upon reaction with HCl in the marine boundary layer will produce FeCl₃. The HCl comes from exchange reaction of sea-salt NaCl with HNO₃ or H₂SO₄ (from NO_x and SO₂ emissions from the combustion processes), producing NaNO₃ or Na₂SO₄ (Finlayson-Pitts 2003).

Key features of the ISA nature-based solution include:

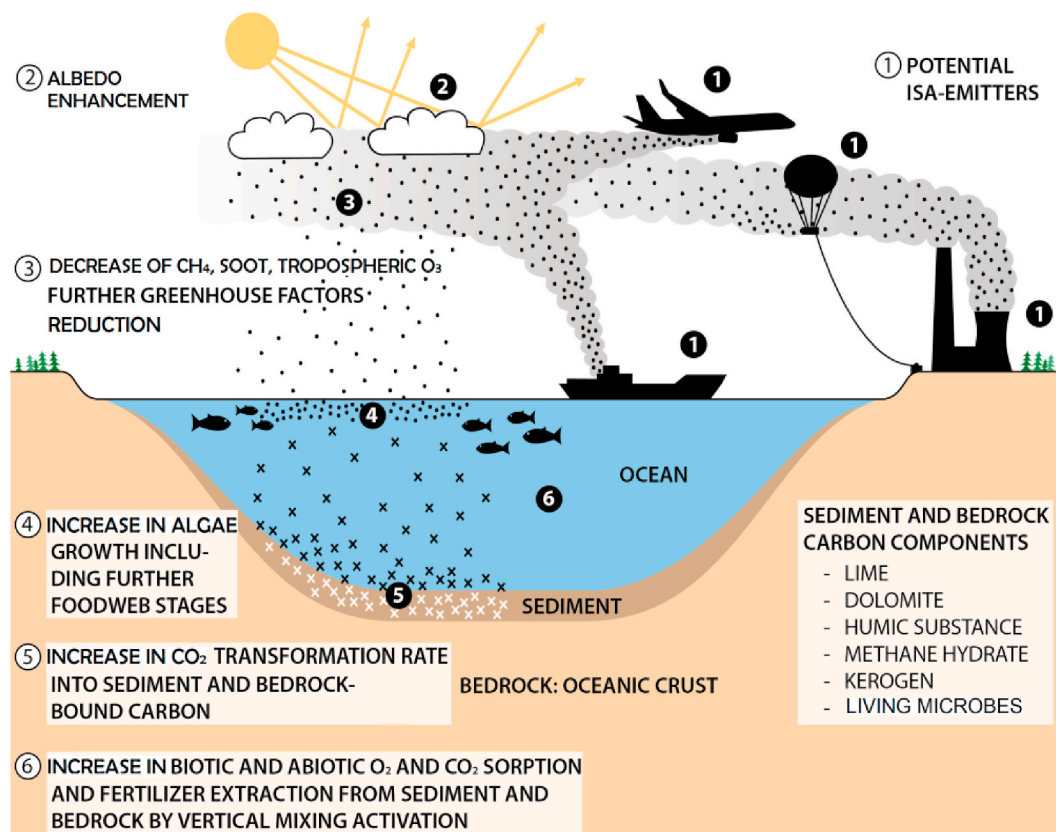


Fig. 1. Suggested methods to enhance Iron Salt Aerosols and principal effects acting on climate change. Reproduced from (Oeste et al., 2017).

- ISA copies the possible natural global cooling process of the ice ages, where iron-rich dust blowing from continents might have been an important cooling amplifier (Fischer et al., 2007; Khatiwala et al., 2019);
- the atmospheric input in ocean surface of soluble ISA from the fossil fuels industry which might already play a significant role in ocean productivity (Rathod et al., 2020);
- iron released in the troposphere, preferably above the boundary layer, will disperse locally but regionally, achieving greater dilution by dispersion over a larger surface area (Ito 2013), probably resulting in better plankton uptake than from surface-based larger OIF;
- iron contained in coal is already released in the hot gas plumes from the stacks of fossil fuel power plants, masking to some level the climate impacts of the carbon emissions in these flue gases (Rathod et al., 2020);
- as chlorine atom generation catalyzed by iron is most effective in the lower troposphere, a range of ISA deployment methods using surface level chimneys or tethered balloons 200 m above the 1 km average tropospheric boundary layer are being considered (Oeste et al., 2017);
- iron can be released by a balloon in a similar way as planned in the "SPICE project" (Kuo et al., 2012), directly sprayed (nebulized) from a solution, or after combustion of an oil in which an iron organic complex is dissolved.

As stated by Williamson et al. (Williamson et al., 2012): "Twenty years ago, iron-based ocean fertilization looked like a highly efficient process. Based on the C:Fe ratio in phytoplankton (Sunda et al. 1991), it was calculated in the best case scenario that each atom of added iron might enable plankton growth using more than 100,000 atoms of carbon. Current estimates are that even the natural (re-)supply of dissolved iron to iron-depleted waters is at least an order of magnitude less efficient (Blain et al. 2007; Pollard et al. 2009), whilst experimental treatments – and natural atmospheric inputs, via dust – seem to be several orders of magnitude less efficient (Boyd et al. 2004; Buesseler et al. 2004; Gabric et al. 2010)". Even at these lower levels of efficacy; iron fertilization by ISA, together with other cooling effects, might be an efficient, rapid and scalable contribution to efforts to slow global warming, provided its safety is proven.

Cost estimates of CDR by ISA are given in Table 1 according to several experimental determinations of the Fe:C molar ratio in plankton communities before or after OIF.

Even recognizing that the C sequestration is only partial, the cost values obtained in table 1 (as low as \$0.10/tCO₂) suggest the ISA method (estimated at ~\$1/tCO₂), if field trials demonstrate its safety, could be the cheapest available Negative Emissions Technology (NET) (McLaren 2012). Its dilute dispersion means ISA has high plankton uptake potential, despite the uncertain amount of carbon that will sink to the bottom of the ocean for long term or permanent removal from the atmosphere. These cost estimates are partial, as they only take into consideration the possible OIF effect of ISA. So overall unit cost per ton of CO₂-eq removed could be lower than these estimates if its additional effects in the troposphere could significantly enhance this cooling effect. In addition, ISA effects should be much more rapid, and the growth of phytoplankton in the upper ocean has the added benefit of increasing ocean biomass and the marine food web, even while it returns some carbon to the air.

Expected ISA cooling effects not taken into consideration for the cost estimations made in Table 1 include tropospheric CH₄ and surface-ozone removal, CH₄ emissions reduction, tropospheric Marine Cloud Brightening by enhanced DMS emissions (Wingenter 2007) and some others (Oeste et al., 2017). Also, as will be seen in the next section, the calculations in the table above only take into account the iron content of phytoplanktonic cells, and not the iron recycling, nor the benefits to the oceanic food-web.

Table 1

ISA Costs. Selected literature indicates C:Fe ratios in plankton during iron fertilization experiments, illustrating the possible extremely low costs of Carbon Dioxide Removal (CDR) by ISA employing an iron organic complex as precursor. These figures assume material and delivery costs of US\$ 35,000/ton of iron as ferrocene. They are for short term CO₂ drawdown, not long-term storage, and do not include the other effects of ISA such as removal of some non-CO₂ GHGs, nor albedo enhancement which could enhance ISA cooling potential (Oeste et al., 2017). The molar ratio of Fe and C is given by Fe/C = 56/12 = 4.65, while the CO₂/C ratio is 44/12 = 3.67, giving a Fe/CO₂ molar ratio of 56/44 = 1.27.

(Author and reference) Text from article	moles C:Fe ratio	tons CO ₂ /1 ton Fe	cost in US\$/ton CO ₂ removal by the ISA method
(Morel and Hudson 1985), (Anderson and Morel 1982), (Martin 1990)	10,000:1 to 100,000:1	1,706,000 to 75,871	\$5/tCO ₂ to \$0.5/tCO ₂
extended Redfield ratio (Liu et al., 2010) 106 Carbon: 16 Nitrogen: 1 Phosphorus: 0.1–0.001 Iron	1,060:1 to 106,000:1	833 to 83,280	\$42/tCO ₂ to \$0.42/tCO ₂
Ho et al. (2003)	124,000:7.5 or 16,533:1	12,990	\$2.65/tCO ₂
Boyd et al. (2004) (Maldonado et al., 2001) intracellular Iron:C ratios of 6.6 μmol iron/mol C	26,000:1 151,515:1	20,428 119,047	\$1.70/tCO ₂ \$0.3/tCO ₂
(Twining et al., 2004) Iron:C ratios of 6.0–14.1 μmol:μmol before iron addition and 40 μmol:μmol after iron addition	166,666:1 25,000:1	130,951 19,643	\$0.265/tCO ₂ then then \$1.80/tCO ₂
(Sarthou et al., 2008) Fe:C ratio mean value of 4.47 μmol:μmol	233,713:1	175,774	\$0.2/tCO ₂
(Abraham et al., 2000) 3 μmol Fe per mol C	333,333:1	261,902	\$0.13/tCO ₂
(Buitenhuis et al., 2016) zooplankton and marine bacteria have a Fe:C ratio of 2.10 ⁻⁶	500,000:1	392,854	\$0.09/tCO ₂

5. Discussion

One of the principal criticisms made of OIF is that only limited amounts of the organic carbon obtained during phytoplankton blooms may reach and stay stored in the deep ocean, because respiration and bacterial degradation of the dead organic matter will rapidly return much of the CO₂ to the atmosphere (Martin et al., 2013; Williamson et al., 2012). In the two next subsections we show new evidence that several mechanisms allow prediction of higher levels of mineral and organic carbon storage, in solid and dissolved forms. In the following subsections we address the potential side-effects of reductions of anthropogenic iron emissions and describe the potential human health risks of ISA emissions.

5.1. The oceanic food web, carbon storage and recycling of iron and other nutrients

The world ocean is more than double the total size of the continents. If on its abundant surface area, natural energy and nutrients can be harnessed, the ocean could become the primary location for efficient carbon removal and cooling methods. ISA could prove a useful and effective ocean cooling method replicating the natural levels of iron that prevailed in the ice ages. However, the complexity of the oceanic food-web scatters and dilutes the organic carbon produced by addition of iron, making it difficult to measure the particle flux and carbon export to the deep ocean. Despite new evidence that of iron-rich dust caused significant reduction in CO₂ and CH₄ levels with effective carbon storage during the glacial periods (Masson-Delmotte et al., 2010; Sigman et al.,

2010; Stoll 2020), some scientists fear that a large part of the organic carbon of OIF phytoplankton blooms will decompose back into CO₂ and return to the atmosphere (Martin et al., 2013). Consequently, part of the scientific community think that carbon sequestration after OIF might be poor or limited to about 1 GtC yr⁻¹ and fear OIF might also release CH₄ and N₂O which are powerful GHGs, offsetting the desired effects of CO₂ sequestration (Bowie et al., 2016).

More than half of all anthropogenic emissions of CO₂ are now stored in ocean and land sinks. The 2006–2015 average emissions from fuels and industry are evaluated at 9.3 ± 0.5 Gt C yr⁻¹ and land emissions (from agriculture, wetlands, etc.) at 1.0 ± 0.5 GtC yr⁻¹. From this total, less than half of the CO₂ emissions accumulate in the atmosphere (atmospheric CO₂ growth of 4.5 ± 0.1 GtC yr⁻¹) (Le Quéré et al., 2016). Land and oceanic primary productivity mean about one quarter of emitted CO₂ is stored in land (land sink of 3.1 ± 0.9 GtC yr⁻¹) and another quarter in the oceans (ocean sink of 2.6 ± 0.5 GtC yr⁻¹) due also to the gas ↔ liquid CO₂ equilibrium between the atmosphere and the ocean. Some computer modeling suggests that to restore pre-industrial levels of atmospheric CO₂ concentrations it will be necessary to remove double the excess CO₂ in the atmosphere, because the oceanic CO₂ will outgas to the atmosphere (Cao and Caldeira 2010). But, most of the oceans' assimilation of carbon is stored in stable compounds (Jiao et al., 2010), preventing faster ocean acidification by dissolved CO₂ and carbonic acid. In the past, massive amounts of organic carbon burial and storage occurred in marine sediments (Raven et al., 2018), and in oxic sub-seafloor sediment as persistent organic matter (Estes et al., 2019).

Marine carbon storage may prove to be well above levels suggested by critics of OIF (Smetacek 2018), due to the complexity of the marine biogeochemical cycle (Chen et al., 2018; Zhang et al., 2018) and the oceanic food web structure, as well as, on a very different scale, the oceanic crustal formation discussed below (subsection 5.2), which is a major permanent active alkalinity source and long-term carbon storage locality.

A great advantage of ISA is that once its safety and efficacy proved, its deployment might become justified by the methane removal effect alone, meaning the range of suggested complex ocean iron effects described below can be examined as expected beneficial side-effects, not as the primary initial project objective.

In open ocean trials in silica-rich regions, OIF expands plankton communities dominated by diatoms, allowing efficient deep carbon export and storage (Smetacek et al., 2012). In silica-depleted regions of the Southern Ocean (SO), OIF experiments found that the plankton community was dominated by flagellates, releasing slow-sinking short-lived fecal pellets. But efficient conversion from lithogenic mineral to biologically available iron by copepods allows efficient iron recycling and results in a large spatial spread and longevity of blooms, as a major driver for recycling of iron in the SO is copepod grazing (Laglera et al., 2017).

Krill eat phytoplankton on the ocean surface, but then the krill swarms dive deep, down to 1000 m, where they defecate and their feces pellets become an important part of the carbon bottom sediment (Tarling and Thorpe 2017). The iron content in krill rises with the amount of ingested lithogenic particles (Schmidt et al., 2016) and this iron remains in the marine food web as krill are eaten. In some laboratory experiments, surprisingly, it is when zooplankton (copepods or rotifers) are added to the cultures that phytoplankton biomass is the highest (Trommer et al., 2012) and on average, the presence of copepods increased the iron regeneration rates by 48% (Sarthou et al., 2008).

Similar mechanisms to the iron recycling processes exist for other important macronutrients (N, P) or micronutrients (Zn). As all species do not have the same overall chemical composition and metabolic needs as their prey, different proportions of the nutrients ingested by zooplankton will be rejected, modifying the composition of the environment by selective recycling of some elements. For instance, copepods are usually less rich in phosphorus and richer in nitrogen than the

phytoplankton they feed on: the P diet excess will be excreted, thereby modifying the N:P ratio in the environment, altering the dynamics of the plankton communities (Trommer et al., 2012). As copepod and rotifer zooplankton groups recycle the nutrients differently, further fertilizations will be more efficient in conditions enriched in N or in P, and after proliferation some species will decline, while others feeding from excreta or from dead bodies of the previous ones will prosper.

Phytoplankton, zooplankton, bacteria, viruses, seaweed, krill, fish, sea-mammals and birds participate in the marine food web, which in turn not only supports human consumption of fish, but also maintains the overall homeostatic stability of the world climate (Watson and Lovelock 1983). The iron in phytoplankton cells is transferred through grazing into the body organs, tissues and muscle of herbivores, to be later consumed and transferred several more times to higher trophic levels (Ratnarajah et al., 2018). Excess iron intake beyond the metabolic demand of pelagic vertebrates is defecated or excreted at large distances from the initial plankton bloom, by fish, whales (Ratnarajah et al., 2017; Ratnarajah et al., 2016), marine mammals (Wing et al., 2014) and seabirds (Wing et al., 2017). Some of their waste products spread at distances far away from the initial plankton bloom containing high concentrations of recycled bioavailable iron which can be used for new phytoplankton fertilization. Improving marine biosystems through effective addition of iron could strengthen their resilience and biodiversity through both cooling and nutrient processes, and in turn also support global food security.

As early as 1971, Smayda (1971) suggested that phytoplankton sinking rates can be accelerated by a range of physical and biological mechanisms in situ (aggregation, packaging of cells in fecal pellets, down-welling and density inversion currents) and this view has since been confirmed (Bach et al., 2016). Typical in-situ carbon export measurements in the oceanic surface layers that detect solid matter (particles and aggregates) sinking by gravity, cannot easily detect dissolved organic matter downward to the mesopelagic level, 200–1000 m below the surface (Stukel et al., 2018).

The role of the ocean as a sink for anthropogenic CO₂ (Sabine et al., 2004) depends not only on the biological pump (Turner 2015), but also on the microbial pump (Jiao and Azam 2011). The biological pump begins with primary producers fixing CO₂ in the upper ocean. The carbon (dissolved organic matter or biogenic particles) then sinks to the deep ocean. Some of it is re-mineralized to CO₂, and stored in deep waters until it is ventilated at the ocean surface over centennial to millennial timescales (England 1995).

Contrary to suggestions of rapid out-gassing, the microbial pump transforms organic matter into refractory dissolved organic C, able to stay thousands of years in seawater. The global ocean's recalcitrant dissolved organic carbon pool is estimated at more than 600 Gt C (Jiao et al., 2018; Jiao et al., 2010).

5.2. The oceanic crust and the bottom sediment

Recent analysis suggests the carbon sequestration resulting from OIF may be much more than critics have argued, with much less deep-sea carbon returning to the atmosphere than previously estimated. In the depths of the oceans, organic carbon, dissolved organic carbon and carbonates are stored in the sediment by several processes (KeLLey et al., 2007; Lartaud et al., 2011).

The scale of ocean crust aquifers is immense. Up to 100 billion m³ of ocean water are driven through the porous ocean crust by thermal up-welling every day (Jørgensen and Zhao 2016). These waters become chemically reduced in their inorganic carbon and salt content by temperatures above 500 °C, alkaline silicates, and sulfate and nitrate reducing conditions. The abundant rock olivine induces carbon precipitation at large scale, generating serpentine, magnetite, hydrogen, heat and a volume expansion (Manuella et al., 2018). The serpentinite reaction can reach depths up to 35 km.

According to Shilobreeva et al. (Shilobreeva et al., 2011) samples

from ocean bottom drilling have shown that within the young oceanic crust, most of the total carbon content can be organic (Proskurowski et al., 2008), transforming HCO_3^- and CO_2 into stable minerals (Manuella et al., 2018).

By these and other processes, organic carbon is fixed in the sediments at the ocean bottom (Observatory, 2018) and within the underlying ocean crust, sequestered by physical and chemical conditions and processes.

One of the most important potential cooling effects of the ISA method is that by cooling the surface of the ocean it activates the vertical cycling of ocean currents as well as the increased physical absorption of O_2 and CO_2 (Oeste et al., 2017), with potential for the additional O_2 to restore suboxic and even some anoxic oceanic regions. This activated transport also moves the dissolved inorganic carbon from the atmosphere to the carbon sinks in the ocean crust and overlying bottom sediment. It also enhances the transport into the deep carbon sinks the carbon generated by the food chain, and dissolved inorganic carbon originating from continental surface run-off.

According to Liu et al. (Liu et al., 2015): "Carbon in rocks and its rate of exchange with the exosphere is the least understood part of the carbon cycle. The amount of carbonate subducted as sediments and ocean crust is poorly known, but essential to mass balance the cycle". This means current accepted estimations of carbon burial within the oceanic crust may be too low, making the potential permanent storage resulting from ISA more significant.

5.3. Side effects of reducing anthropogenic iron emissions

Numerous studies suggest that iron dust fertilization in the Southern Ocean (SO) during the last million years caused up to half of each cyclic 80–100 ppm decrease of tropospheric CO_2 during glacial cycles (Martínez-García et al., 2011). During glacial periods, dust deposition in the SO was 3–5 times greater than during the warmer periods (the interglacials) (Lamy et al., 2014) mainly because the continents were drier. As well, due to glacial physical weathering the flux of soluble iron was enhanced by ~15–20 times in the coldest periods compared with interglacials (Shoenfelt et al., 2018). As noted above, a side effect of cutting emissions from combustion processes might be to reduce ocean iron levels even further from their current low level. An effective approach for cooling must probably put back more iron than is removed. An important factor in calculating the climate impact of fossil fuel emission reduction is that anthropogenic Fe aerosols is today a major source of bioavailable Fe to the oceans (Lin et al., 2015).

Artificial OIF experiments in HNLC regions provided evidence that phytoplankton blooms are generated by iron addition and can produce efficient C-export and storage in the deep ocean (Smetacek et al., 2012). The observation of natural iron phytoplankton blooms induced by continental dust fertilization (Martínez-García and Winckler 2015), volcanic ash (Duggen et al., 2007), melting icebergs (Duprat et al., 2016), krill seabed foraging (Schmidt et al., 2011) and the upwelling of iron-rich deep waters (Blain et al., 2008), as well as short-term in situ experiments of artificial iron enrichment, conducted in different HNLC regions of the oceans up to 2009 (Yoon et al., 2018) allowed researchers to study the effects of iron on marine productivity and ecosystem structure.

For a significant portion of Northern Hemisphere oceans, about 50% of the soluble iron supply is due to human activities, according to model results (Ito and Shi 2016).

In the northern Pacific and northern Atlantic Oceans, the high iron emissions from combustion processes suggests larger inputs of soluble Fe of anthropogenic origin, than in the southern hemisphere which is likely to enhance the net primary productivity in those regions (Wang et al., 2015a; Wang et al., 2015b).

Some models estimate the current anthropogenic iron emissions to be about 3 times higher than for 1850, but project by year 2100 a 5-fold decrease (Myriokefalitakis et al., 2015) based on transition away from

fossil fuels and clean air standards.

In order to better predict the anthropogenic perturbations to oceanic nutrient biogeochemistry, the tropospheric fluxes of labile iron to the open oceans should consider iron-containing aerosols from both natural lithogenic and pyrogenic sources (Ito et al., 2019).

Climate change could reduce desert dust sources of iron, while new regulations aimed to improve health and air quality could reduce the soluble fraction of iron transported to the oceans by reducing acid and mineral emissions from the chimneys of fossil fuel power plants (Li et al., 2017).

Let us imagine what could possibly happen if all the coal emissions ended, stopping its iron, nitrogen oxides, sulfate as well as CO_2 emissions. Although not all NO_x , sulphates and iron emissions will be stopped, possible consequences of their reduction could be that:

- lower levels of aerosols with cooling effects would be produced: this will be very good for the health of living organisms but might have some bad effects for climate: inducing global warming (Samset et al., 2018; Six et al., 2013), with estimated surface heating global mean of 0.5–1.1 °C if all those pollutants were removed;
- global primary productivity could decrease (Li et al., 2017) over the continents, which would probably receive less phosphorus (Wang et al., 2015c), iron and nitrogen oxides, although perhaps not immediately in the oceans, because the iron dust accumulated on the glaciers and polar ice caps is now progressively reaching the oceans because of ice melting.
- soils and microorganisms would possibly release more CH_4 into the atmosphere that would stay there longer, because the reduced iron amounts in the atmosphere destroy less CH_4 and because lower sulfur deposition will also enhance CH_4 emissions (Gauci et al., 2008; Jäckel et al., 2005).

Reducing anthropogenic iron aerosol emissions (Li et al., 2017) and sulfuric acidic pollution (Samset et al., 2018) could provide very important health benefits through elimination of co-emitted pollution, but with serious climate counter-effects (Sofiev et al., 2018).

Deliberate addition of soluble iron to the atmosphere might be a remedy for this unwanted effect that should be tested, and if its safety is proved, should be deployed in order to counteract or outweigh the expected negative climate effects of the removal of iron involved in decarbonizing the economy.

5.4. Possible human health impact effects of iron salts

While iron particles can be toxic in some chemical forms, oxidation states and depend on the mode of exposure (Baek et al., 2020; Pease et al., 2016), there are many biomedical applications of iron oxide nanoparticles (Wu et al., 2015) and iron is an essential element for human health, with iron deficiency causing anemia and several disorders (Abbaspour et al., 2014; Aspuru et al., 2011).

- a) To minimize health risks, initial ISA release should be over oceans and remote areas. Human inhalation would be a tiny fraction of existing levels from iron dust and iron pollution (Seaton et al., 2005; Smith et al., 2020). Even for workers on ships or platforms that generate the ISA, the height of release and the wind direction and intensity should be sufficient to prevent inhalation, and emissions need to be rapidly diluted by wind or ship movement. ISA from ships or platforms should only occur during suitable weather conditions.
- b) Natural desert dust emissions contain iron and quartz and during storms can distribute thousands of times more iron than the envisaged amount of ISA. These natural iron emissions are localized and occur in short episodes and periods, in contrast to ISA planned regular release in very dilute form, over numerous well distributed locations, mainly over remote regions of Southern Ocean, and if proven efficient potentially to remove methane buildup in the Arctic.

Potential dust inhalation (containing iron and quartz) is orders of magnitude higher for desert dust than for ISA as it is planned. Of course, more complete safety and environmental impact assessments are necessary before any deployment.

- c) We propose that ISA should provide the same mass of iron emissions as current anthropogenic iron emissions from combustion processes (Chaulya et al., 2019). But whereas these existing emissions cause pollution in populated areas, ISA emissions would be offshore over regions without inhabitants, with negligible human effects. Farmers use large quantities of iron sulfate and other iron chelates in order to fight iron deficiency induced plant chlorosis and increase crops and fruits production yields. Those iron compounds are authorized for organic farming and are often sprayed over the crops or the orchards (Abadía et al., 2001). Iron emissions are not listed as a significant health problem. A 2017 review of the “*Human health and environmental impacts of coal combustion and post-combustion wastes*” makes no mention of negative impacts of iron (Munawer 2018). For the world oceanic HNLC, to obtain its iron from controlled ISA release would be far better than from fossil fuel burning and industrial processes that also release toxic compounds and heavy metals such as arsenic, lead, mercury, cadmium, etc. ISA generation, is proved safe, would deploy iron with highly regulated purity.
- d) Atmospheric metal levels are already high in cities as a byproduct of vehicular transport, such as from brake abrasion and trains and tramways friction on the rails (Aksu 2015; Seaton et al., 2005; Smith et al., 2020).
- e) Fuel additives containing iron (ferrocene, iron picrate ...) are commercially available, registered and authorized (EPA 2019; Wikipedia 2018) and can “legally” release iron oxides in urban areas upon combustion. These additives are intended to improve health by reducing pollution from soot and BC emissions (Kim et al., 2008). Also bunker fuel for ships contains some iron which generates iron aerosols over the ocean (Ito 2013).
- f) As the iron salt aerosol will be released over the oceans below or just above the marine boundary layer, it will act as cloud condensing nuclei and with humidity the atmospheric life time will be short. Rained-out ISA will mainly be in soluble form (chlorine salt, oxalate complex (Paris and Desboeufs 2013), etc.) with very low risk of inhalation and storage in the lungs in an insoluble form.

We estimate that full deployment of ISA would increase iron oxide particles ‘available’ for inhalation close to urban areas by less than one part per million, overwhelmed by desert dust and transport and energy sector emissions (Mahowald et al., 2009). Against this, the potential cooling impact of a scaled ISA program could deliver major health benefits, reducing the likelihood of further climate tipping points being reached.

6. Conclusions

The natural elimination of GHGs other than CO₂ in the atmosphere mainly results from reaction with the °OH radical and sunlight photolysis. Evidence that photocatalysis can enhance the speed of destruction of GHGs is well known (de Richter and Caillol 2011). More and more evidence is accumulating that diverse reactions occur on mineral dust aerosols in the atmosphere (Chen et al., 2011; Cwiertny et al., 2008; George et al., 2015). Iron(III)/iron(II) photocatalytic inducement of halogen atoms in the troposphere has been experimentally verified (Wittmer et al., 2016).

A nature-based method has been described in this article: proposing the use of ISA to enhance the amount of tropospheric Cl[•] in order to destroy CH₄, some surface tropospheric O₃ and some soot-BC, and then remove some CO₂ by diluted OIF; and cool the Earth by several other mechanisms such as producing DMS which will in turn act by MCB effect (Wingenter 2007).

In view of the risks of climate tipping points such as further melting

of polar and subpolar glaciers, and potential massive release of methane by destabilization of oceanic methane hydrates or melting permafrost (Lenton et al., 2019; O’Connor et al., 2010), to our knowledge the ISA nature-based solution and photocatalytic processes (de Richter et al., 2017; Tang et al., 2019) are the only proposed methods that may enhance the speed of atmospheric CH₄ removal. ISA might also reduce or inhibit CH₄ emissions (Hu et al., 2020; Jäckel and Schnell 2000), while also mitigating other factors that increase the danger of tipping points (Lenton et al., 2019). In case the safety of the ISA “nature-based” method has successfully been proved, iron compounds in the atmosphere may help remove methane in an efficient way.

In the near future, cuts to fossil fuel emissions and higher air quality standards, aimed to improve air quality and human health and slow-down climate change, are expected to reduce aerosol emissions and thus atmospheric deposition of nutrients, among them iron, with strong potential to inadvertently accelerate the decline of oceanic productivity and increase the global warming factor caused by absence of iron aerosols.

Although some oceanic compensation will occur by release of dust containing iron from melting glaciers and icebergs (Raiswell et al., 2016), reduction in anthropogenic emissions from combustion processes will increase atmospheric GHGs levels through reduction of:

- terrestrial iron fertilization (Li et al., 2017);
- the tropospheric methane sink provided by the chlorine radical, which is part of an iron(III)/iron(II) photo-catalyzed cycle (Wittmer et al., 2016);
- iron deposition and sulfate deposition over wetlands and humid landscapes (Gauci et al., 2004; Jäckel and Schnell 2000).

Fortunately, rapid progress in the fight to mitigate global warming can be expected thanks to the development of a portfolio of NETs, which all deserve to be fully evaluated and assessed.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Tz Ming and S Caillol declare that they have no conflict of interest. R K de-Richter declare being member of NGO <https://restoreourclimate.earth/> no financial interest. R. Tulip declare being webmaster of <http://www.ironsaltaerosol.com/> no financial interest. F D Oeste declare holding patent WO/2010/075856 “Method for cooling the troposphere” and member of NGO <https://restoreourclimate.earth/>.

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List of abbreviations

AR5	5th assessment report
BC	Black Carbon
DMS	dimethyl sulfide
GHG	greenhouse gas

HNLC	high-nutrient low-chlorophyll
IPCC	intergovernmental panel on climate change
ISA	iron salt aerosol
MCB	marine cloud brightening
NET	negative emissions technology
OIF	ocean iron fertilization
VOC	volatile organic compound

Author contributions

Tz Ming: Conceptualization, Writing – original draft preparation, Funding acquisition, Supervision. R de Richter: Conceptualization, Bibliography, Writing – original draft preparation, Supervision. F D Oeste: Conceptualization. R. Tulip: Reviewing and Editing, Structuring. S. Caillol: Writing – original draft preparation.

References

- Abadi, Mehrdad S., et al., 2020. Atmospheric dust stimulated marine primary productivity during Earth's penultimate icehouse. *Geology* 48 (3), 247–251.
- Abadia, J., et al., 2001. Correction of iron chlorosis by foliar sprays. *International Symposium on Foliar Nutrition of Perennial Fruit Plants* 115–121, 2001.
- Abadia, Javier, et al., 2011. Towards a knowledge-based correction of iron chlorosis. *Plant Physiol. Biochem.* 49 (5), 471–482.
- Abbaspour, Nazanin, Hurrell, Richard, Kelihsadi, Roya, 2014. Review on iron and its importance for human health. *J. Res. Med. Sci.* 19 (2).
- Abraham, Edward R., et al., 2000. Importance of stirring in the development of an iron-fertilized phytoplankton bloom. *Nature* 407 (6805), 727.
- Aksu, Abdullah, 2015. Sources of metal pollution in the urban atmosphere (A case study: tuzla, Istanbul). *Journal of Environmental Health Science Engineering* 13 (1), 1–10.
- Ali, Muhammad Aslam, Chang, Hoon Lee, Kim, Pil Joo, 2008. Effect of silicate fertilizer on reducing methane emission during rice cultivation. *Biol. Fertil. Soils* 44 (4), 597–604.
- Allan, W., Struthers, H., Lowe, D.C., 2007. Methane carbon isotope effects caused by atomic chlorine in the marine boundary layer: global model results compared with Southern Hemisphere measurements. *J. Geophys. Res.: Atmosphere* 112 (D4), 1984–2012.
- Allen, Trilles R., et al., 2009. Warming caused by cumulative carbon emissions towards the trillionth tonne. *Nature* 458 (7242), 1163–1166.
- Anderson, Kevin, 2016. Duality in climate science. *Nat. Geosci.* 8 (12), 898–900.
- Anderson, Michael A., Morel, Francois MM., 1982. The influence of aqueous iron chemistry on the uptake of iron by the coastal diatom *Thalassiosira weissflogii*. *Limnol. Oceanogr.* 27 (5), 789–813.
- Anenberg, Susan C., et al., 2010. An estimate of the global burden of anthropogenic ozone and fine particulate matter on premature human mortality using atmospheric modeling. *Environ. Health Perspect.* 118 (9), 1189.
- Aspuru, Kattalin, et al., 2011. Optimal management of iron deficiency anemia due to poor dietary intake. *Int. J. Gen. Med.* 4, 741.
- Bach, Lennart T., et al., 2016. Influence of plankton community structure on the sinking velocity of marine aggregates. *Global Biogeochem. Cycles* 30 (8), 1145–1165.
- Baek, Kyung-Min, et al., 2020. Characterization and health impact assessment of hazardous air pollutants in residential areas near a large iron-steel industrial complex in Korea. *Atmospheric Pollution Research* 11 (10), 1754–1766.
- Baker, Angela K., et al., 2011. Investigation of chlorine radical chemistry in the Eyjafjallajökull volcanic plume using observed depletions in non-methane hydrocarbons. *Geophys. Res. Lett.* 38 (13).
- Basar, H., et al., 2014. Effect of foliar iron applications on contents of iron forms and mineral composition of sweet cherry (*Prunus avium* L.). *Indo Am. J. Agric. Vet. Sci.* 2 (3), 1–11.
- Blain, Stéphane, et al., 2007. Effect of natural iron fertilization on carbon sequestration in the Southern Ocean. *Nature* 446 (7139), 1070.
- Blain, Stéphane, Sarthou, Géraldine, Laan, Patrick, 2008. Distribution of dissolved iron during the natural iron-fertilization experiment KEOPS (Kerguelen Plateau, Southern Ocean). *Deep Sea Res. Part II Top. Stud. Oceanogr.* 55 (5–7), 594–605.
- Blasing, T., 2016. Recent Greenhouse Gas Concentrations. Carbon Dioxide Information Analysis Center CDIA. 2016. <https://doi.org/10.3334/CDIAC/atg.032>. https://cdia.cess-dive.lbl.gov/pns/current_ghg.html. (Accessed 28 December 2020).
- Bowie, Andrew R., et al., 2016. Position Analysis: Ocean Fertilisation. Antarctic Climate & Ecosystems Cooperative Research Centre. http://acecrc.org.au/wp-content/uploads/2016/07/ACE106_Position-Analysis_Ocean-Fert_April-2016_WEB.pdf. (Accessed 30 March 2018).
- Boyd, Philip W., Bressac, Matthieu, 2016. Developing a test-bed for robust research governance of geoengineering: the contribution of ocean iron biogeochemistry. *Phil. Trans. R. Soc. A* 374 (2081), 20150299.
- Boyd, Philip W., et al., 2004. The decline and fate of an iron-induced subarctic phytoplankton bloom. *Nature* 428 (6982), 549.
- Boyd, P.W., Trull, T.W., 2007. Understanding the export of biogenic particles in oceanic waters: is there consensus? *Prog. Oceanogr.* 72 (4), 276–312.
- Buesseler, Ken O., et al., 2004. The effects of iron fertilization on carbon sequestration in the Southern Ocean. *Science* 304 (5669), 414–417.
- Buitenhuis, Erik T., et al., 2016. Role of zooplankton dynamics for Southern Ocean phytoplankton biomass and global biogeochemical cycles. *Biogeosciences* 13 (14), 4111.
- CA&NCI, 2019. Climate-Analytics, and New-Climate-Institute, the Climate Action Tracker, Warming Projections Global Update. https://climateactiontracker.org/documents/698/CAT_2019-12-10_BriefingCOP25_WarmingProjectionsGlobalUpdate_Dec2019.pdf. (Accessed 24 December 2019).
- Cao, Long, Caldeira, Ken, 2010. Atmospheric carbon dioxide removal: long-term consequences and commitment. *Environ. Res. Lett.* 5 (2), 024011.
- Chaulya, S.K., et al., 2019. Air quality modelling for prediction of dust concentrations in iron ore mines of Saranda region, Jharkhand, India. *Atmospheric Pollution Research* 10 (3), 675–688.
- Chen, Haihan, et al., 2011. Heterogeneous photochemistry of trace atmospheric gases with components of mineral dust aerosol. *J. Phys. Chem.* 115 (4), 490–499.
- Chen, Jing M., Legendre, Louis, Benner, Ronald, 2018. A recent project shows that the microbial carbon pump is a primary mechanism driving ocean carbon uptake. *National Science Review* nwy006.
- Chisholm, S.W., Falkowski, P.G., Cullen, J.J., 2002. Response to the letter of Johnson, K. S. and Karl, D.M. *Science* 296 (5567), 467–468.
- Cwierny, David M., Young, Mark A., Grassian, Vicki H., 2008. Chemistry and photochemistry of mineral dust aerosol. *Annu. Rev. Phys. Chem.* 59, 27–51.
- De Baar, Hein, J.W., et al., 2005. Synthesis of iron fertilization experiments: from the iron age in the age of enlightenment. *J. Geophys. Res.: Oceans* 110 (C9).
- de Baar, Hein, J.W., et al., 2008. Efficiency of carbon removal per added iron in ocean iron fertilization. *Mar. Ecol. Prog. Ser.* 364, 269–282.
- de Richter, R., Caillol, S., Ming, T., 2018. Geo-Engineering: Sunlight Reflection Methods and Negative Emissions Technologies for Greenhouse Gas Removal, Chapter 20 in *Managing Global Warming*, Trevor Letcher. Elsevier.
- de Richter, Renaud, Caillol, Sylvain, 2011. Fighting global warming: the potential of photocatalysis against CO₂, CH₄, N₂O, CFCs, tropospheric O₃, BC and other major contributors to climate change. *J. Photochem. Photobiol. C Photochem. Rev.* 12 (1), 1–19.
- de Richter, Renaud, et al., 2017. Removal of non-CO₂ Greenhouse Gases by Large-Scale Atmospheric Solar Photocatalysis. *Progress in Energy and Combustion Science*. Submitted.
- Deguillaume, Laurent, Leriche, Maud, Chaumerliac, Nadine, 2005. Impact of radical versus non-radical pathway in the Fenton chemistry on the iron redox cycle in clouds. *Chemosphere* 60 (5), 718–724.
- Denman, Kenneth L., 2008. Climate change, ocean processes and ocean iron fertilization. *Mar. Ecol. Prog. Ser.* 364, 219–225.
- Ding, Xiang, et al., 2020. Gaseous and particulate chlorine emissions from typical iron and steel industry in China. *J. Geophys. Res.: Atmosphere* 125 (15), e2020JD032729.
- Duggen, Svend, et al., 2007. Subduction zone volcanic ash can fertilize the surface ocean and stimulate phytoplankton growth: evidence from biogeochemical experiments and satellite data. *Geophys. Res. Lett.* 34 (1).
- Duprat, L.P., Grant, R.B., Wilton, D.J., 2016. Enhanced Southern Ocean marine productivity due to fertilization by giant icebergs. *Nat. Geosci.* 9 (3), 219–221.
- EASAC, 2018. European Academies Science Advisory Council. Negative Emissions Technologies: what Role in Meeting Paris Agreement Targets? Schaefer Druck und Verlag GmbH, Teutschenthal, Germany, ISBN 978-3-8047-3841-6. https://easac.eu/fileadmin/PDF_s/reports_statements/Negative_Carbon/EASAC_Report_on_Negative_Emission_Technologies.pdf. (Accessed 30 March 2018).
- El-Jendoubi, Hamdi, et al., 2014. The effects of foliar fertilization with iron sulfate in chlorotic leaves are limited to the treated area. A study with peach trees (*Prunus persica* L. Batsch) grown in the field and sugar beet (*Beta vulgaris* L.) grown in hydroponics. *Front. Plant Sci.* 5, 2.
- Elwardany, Ahmed E., et al., 2020. Improving performance and emissions characteristics of compression ignition engine: effect of ferrocene nanoparticles to diesel-biodiesel blend. *Fuel* 270, 117574.
- Emerson, David, 2019. Biogenic iron dust: a novel approach to ocean iron fertilization as a means of large scale removal of carbon dioxide from the atmosphere. *Frontiers in Marine Science* 6, 22.
- England, Matthew H., 1995. The age of water and ventilation timescales in a global ocean model. *J. Phys. Oceanogr.* 25 (11), 2756–2777.
- EPA, 2019. Alphabetical List of Registered Gasoline and Diesel Additives. United States Environmental Protection Agency. <https://www3.epa.gov/otaq/fuels1/fuars/web-addt.htm>. (Accessed 10 February 2019).
- Estes, Emily R., et al., 2019. Persistent organic matter in oxic subseafloor sediment. *Nat. Geosci.* 1.
- Fernández, Victoria, Sotiropoulos, Thomas, H Brown, Patrick, 2013. Foliar Fertilization: Scientific Principles and Field Practices: International Fertilizer Industry Association.
- Finlayson-Pitts, B.J., 1993. Chlorine atoms as a potential tropospheric oxidant in the marine boundary layer. *Res. Chem. Intermed.* 19 (3), 235–249.
- Finlayson-Pitts, B.J., 2003. The tropospheric chemistry of sea salt: a molecular-level view of the chemistry of NaCl and NaBr. *Chem. Rev.* 103 (12), 4801–4822.
- Fischer, Hubertus, et al., 2007. Glacial/interglacial changes in mineral dust and sea-salt records in polar ice cores: sources, transport, and deposition. *Rev. Geophys.* 45 (1).
- Gabric, A.J., et al., 2010. Australian dust storms in 2002–2003 and their impact on Southern Ocean biogeochemistry. *Global Biogeochem. Cycles* 24 (2).
- Gauci, Vincent, et al., 2008. Halving of the northern wetland CH₄ source by a large Icelandic volcanic eruption. *J. Geophys. Res.: Biogeosciences* 113 (G3).
- Gauci, Vincent, et al., 2004. Sulfur pollution suppression of the wetland methane source in the 20th and 21st centuries. *Proc. Natl. Acad. Sci. Unit. States Am.* 101 (34), 12583–12587.

- George, Christian, et al., 2015. Heterogeneous photochemistry in the atmosphere. *Chem. Rev.* 115 (10), 4218–4258.
- Grandey, Benjamin S., Wang, C., 2015. Enhanced marine sulphur emissions offset global warming and impact rainfall. *Sci. Rep.* 5, 13055.
- Guo, Yangyang, et al., 2017. Chemical profiles of PM emitted from the iron and steel industry in northern China. *Atmos. Environ.* 150, 187–197.
- Güssow, Kerstin, et al., 2010. Ocean iron fertilization: why further research is needed. *Mar. Pol.* 34 (5), 911–918.
- Gustafsson, Örjan, Ramanathan, Veerabhadran, 2016. Convergence on climate warming by black carbon aerosols. *Proc. Natl. Acad. Sci. Unit. States Am.* 113 (16), 4243–4245.
- Hamilton, Douglas S., et al., 2020. Impact of changes to the atmospheric soluble iron deposition flux on ocean biogeochemical cycles in the Anthropocene. *Global Biogeochem. Cycles* 34 (3), e2019GB006448.
- Harvey, Hal, Orr Jr., Franklin M., Vondrich, Clara, 2013. A trillion tons. *Daedalus* 142 (1), 8–25.
- He, Zhanfei, et al., 2018. Microbiological and environmental significance of metal-dependent anaerobic oxidation of methane. *Sci. Total Environ.* 610, 759–768.
- Heinemann, Malte, Segsneider, Joachim, Schneider, Birgit, 2019. CO₂ drawdown due to particle ballasting by glacial aeolian dust: an estimate based on the ocean carbon cycle model MPIOM/HAMOCC version 1.6. 2p3. *Geosci. Model Dev. (GMD)* 12 (5), 1869–1883.
- Herzog, Howard J., 2011. Scaling up carbon dioxide capture and storage: from megatons to gigatons. *Energy Econ.* 33 (4), 597–604.
- Ho, Tung-Yuan, et al., 2003. The elemental composition of some marine phytoplankton. *J. Phycol.* 39 (6), 1145–1159.
- Hossaini, Ryan, et al., 2016. A global model of tropospheric chlorine chemistry: organic versus inorganic sources and impact on methane oxidation. *J. Geophys. Res.: Atmosphere* 121 (23), 14,271–14,297.
- Hu, Jinli, et al., 2020. Ferrous iron addition decreases methane emissions induced by rice straw in flooded paddy soils. *ACS Earth Space Chemistry* 4 (6), 843–853.
- Indermühle, Andreas, et al., 1999. Early Holocene atmospheric CO₂ concentrations. *Science* 286 (5446), 1815–1815.
- Ito, A., Shi, Z., 2015. Delivery of anthropogenic bioavailable iron from mineral dust and combustion aerosols to the ocean. *Atmos. Chem. Phys. Discuss.* 15 (16), 23051–23088.
- Ito, Akinori, 2013. Global modeling study of potentially bioavailable iron input from shipboard aerosol sources to the ocean. *Global Biogeochem. Cycles* 27 (1), 1–10.
- Ito, Akinori, et al., 2019. Pyrogenic iron: the missing link to high iron solubility in aerosols. *Science advances* 5 (5), eaau7671.
- Ito, Akinori, Shi, Zongbo, 2016. Delivery of anthropogenic bioavailable iron from mineral dust and combustion aerosols to the ocean. *Atmos. Chem. Phys.* 16 (1), 85–99.
- Ito, Akinori, et al., 2020. Responses of ocean biogeochemistry to atmospheric supply of lithogenic and pyrogenic iron-containing aerosols. *Geol. Mag.* 157 (5), 741–756.
- Jäckel, Udo, Russo, Salvatore, Schnell, Sylvia, 2005. Enhanced iron reduction by iron supplementation: a strategy to reduce methane emission from paddies. *Soil Biol. Biochem.* 37 (11), 2150–2154.
- Jäckel, Udo, Schnell, Sylvia, 2000. Suppression of methane emission from rice paddies by ferric iron fertilization. *Soil Biol. Biochem.* 32 (11–12), 1811–1814.
- Jacobson, Mark Z., 2001. Strong radiative heating due to the mixing state of black carbon in atmospheric aerosols. *Nature* 409 (6821), 695.
- Jia, Jia, et al., 2018. Emission characteristics and chemical components of size-segregated particulate matter in iron and steel industry. *Atmos. Environ.* 182, 115–127.
- Jiao, Nianzhi, Azam, Farooq, 2011. Microbial carbon pump and its significance for carbon sequestration in the ocean. *Microbial Carbon Pump in the Ocean* 10, 43–45.
- Jiao, N., et al., 2018. Unveiling the enigma of refractory carbon in the ocean. *National Science Review* 5 (4), 459–463.
- Jiao, N., et al., 2010. Microbial production of recalcitrant dissolved organic matter: long-term carbon storage in the global ocean. *Nat. Rev. Microbiol.* 8 (8), 593–599.
- Johnson, K.S., Karl, David M., 2002. Is ocean fertilization credible and creditable? *Science* 296 (5567), 467–468.
- Jørgensen, S.L., Zhao, Rui, 2016. Microbial inventory of deeply buried oceanic crust from a young ridge flank. *Front. Microbiol.* 7, 820. <https://doi.org/10.3389/fmicb.2016.00820>.
- Kasper, M., et al., 1999. The influence of fuel additives on the formation of carbon during combustion. *J. Aerosol Sci.* 30 (2), 217–225.
- KeLley, D., et al., 2007. The Lost City hydrothermal field revisited. *Oceanography* 20 (4), 90–99.
- Khatiwala, Samar, Schmittner, A., Juan Muglia, 2019. Air-sea disequilibrium enhances ocean carbon storage during glacial periods. *Science advances* 5 (6), eaaw4981.
- Kim, K.B., Masiello, K.A., Hahn, D.W., 2008. Reduction of soot emissions by iron pentacarbonyl in isoctane diffusion flames. *Combust. Flame* 154 (1–2), 164–180.
- Köhler, Peter, et al., 2010. What caused Earth's temperature variations during the last 800,000 years? Data-based evidence on radiative forcing and constraints on climate sensitivity. *Quat. Sci. Rev.* 29 (1–2), 129–145.
- Kuo, Kristy, A., Watson, I.M., Hugh, EM Hunt, 2012. The SPICE project: an example of geoengineering research. *Water and Climate: policy Implementation Challenges*. In: Proceedings of the 2nd Practical Responses to Climate Change Conference, 2012. Engineers Australia, p. 479.
- Laglera, Luis M., et al., 2017. Iron partitioning during LOHAFEX: copepod grazing as a major driver for iron recycling in the Southern Ocean. *Mar. Chem.* 196, 148–161.
- Lalonde, Karine, et al., 2012. Preservation of organic matter in sediments promoted by iron. *Nature* 483 (7388), 198–200.
- Lamy, Frank, et al., 2014. Increased dust deposition in the Pacific Southern Ocean during glacial periods. *Science* 343 (6169), 403–407.
- Lartaud, Franck, et al., 2011. Fossil evidence for serpentinization fluids fueling chemosynthetic assemblages. *Proc. Natl. Acad. Sci. Unit. States Am.* 108 (19), 7698–7703.
- Latham, John, et al., 2012. Marine cloud brightening. *Phil. Trans. Roy. Soc. Lond.: Mathematical, Physical and Engineering Sciences* 370 (1974), 4217–4262.
- Lawler, M.J., et al., 2009. Pollution-enhanced reactive chlorine chemistry in the eastern tropical Atlantic boundary layer. *Geophys. Res. Lett.* 36 (8).
- Le Quéré, Corinne, et al., 2016. Global carbon budget 2016. *Earth Syst. Sci. Data* 8 (2), 605–649.
- Lenton, Timothy M., et al., 2019. Climate Tipping Points—Too Risky to Bet against. Nature Publishing Group.
- Levine, James G., et al., 2011. The role of atomic chlorine in glacial-interglacial changes in the carbon-13 content of atmospheric methane. *Geophys. Res. Lett.* 38 (4).
- Li, Weijun, et al., 2017. Air pollution–aerosol interactions produce more bioavailable iron for ocean ecosystems. *Science advances* 3 (3), e1601749.
- Lin, Yi-Chiu, et al., 2015. Atmospheric iron deposition in the northwestern Pacific Ocean and its adjacent marginal seas: the importance of coal burning. *Global Biogeochem. Cycles* 29 (2), 138–159.
- Lipson, David A., et al., 2010. Reduction of iron (III) and humic substances plays a major role in anaerobic respiration in an Arctic peat soil. *J. Geophys. Res.: Biogeosciences* 115 (G4).
- Liu, Boming, et al., 2019. The relationship between black carbon and atmospheric boundary layer height. *Atmospheric Pollution Research* 10 (1), 65–72.
- Liu, Deng, et al., 2016. Inhibitory effect of clay mineral on methanogenesis by *Methanosarcina mazei* and *Methanothermobacter thermautotrophicus*. *Appl. Clay Sci.* 126, 25–32.
- Liu, Ke, et al., 2021. The atmospheric iron variations during 1950–2016 recorded in snow at Dome Argus, East Antarctica. *Atmos. Res.* 248, 105263.
- Liu, Kon-kee, et al., 2010. Carbon and Nutrient Fluxes in Continental Margins: a Global Synthesis. Springer Science & Business Media.
- Liu, Shuwei, et al., 2012. Fe (III) fertilization mitigating net global warming potential and greenhouse gas intensity in paddy rice-wheat rotation systems in China. *Environ. Pollut.* 164, 73–80.
- Liu, Yongsheng, et al., 2015. First direct evidence of sedimentary carbonate recycling in subduction-related xenoliths. *Sci. Rep.* 5, 11547.
- Luo, Chao, et al., 2008. Combustion iron distribution and deposition. *Global Biogeochem. Cycles* 22 (1).
- Maher, B.A., et al., 2010. Global connections between aeolian dust, climate and ocean biogeochemistry at the present day and at the last glacial maximum. *Earth Sci. Rev.* 99 (1), 61–97.
- Mahowald, Natalie M., et al., 2009. Atmospheric iron deposition: global distribution, variability, and human perturbations. *Annual Review of Marine Science* 1, 245–278.
- Maldonado, Maria T., et al., 2001. Iron uptake and physiological response of phytoplankton during a mesoscale Southern Ocean iron enrichment. *Limnol. Oceanogr.* 46 (7), 1802–1808.
- Manuella, Fabio C., Scribano, Vittorio, Carbone, Serafina, 2018. Abyssal serpentinites as gigantic factories of marine salts and oil. *Mar. Petrol. Geol.* <https://doi.org/10.1016/j.marpetgeo.2018.03.026> (in press).
- Martin, John H., 1990. Glacial-interglacial CO₂ change: the Iron hypothesis. *Paleoceanography* 5 (1), 1–13.
- Martin, John H., et al., 1994. Testing the iron hypothesis in ecosystems of the equatorial Pacific Ocean. *Nature* 371 (8), 123–129.
- Martin, Patrick, et al., 2013. Iron fertilization enhanced net community production but not downward particle flux during the Southern Ocean iron fertilization experiment LOHAFEX. *Global Biogeochem. Cycles* 27 (3), 871–881.
- Martínez-García, Alfredo, et al., 2011. Southern Ocean dust-climate coupling over the past four million years. *Nature* 476 (7360), 312–315.
- Martínez-García, Alfredo, Winckler, Gisela, 2015. Iron fertilization in the glacial ocean. *DUST* 24, 82.
- Martínez-García, Alfredo, et al., 2009. Links between iron supply, marine productivity, sea surface temperature, and CO₂ over the last 1.1 Ma. *Paleoceanography* 24 (1).
- Masson-Delmotte, Valérie, et al., 2010. EPICA Dome C record of glacial and interglacial intensities. *Quat. Sci. Rev.* 29 (1), 113–128.
- McLaren, Duncan, 2012. A comparative global assessment of potential negative emissions technologies. *Process Saf. Environ. Protect.* 90 (6), 489–500.
- Miller, Kimberley E., et al., 2015. Methane suppression by iron and humic acids in soils of the Arctic Coastal Plain. *Soil Biol. Biochem.* 83, 176–183.
- Morel, F.M.M., Hudson, R.J.M., 1985. The geobiological cycle of trace elements in aquatic systems: redfield revisited. In: Stumm, E. (Ed.), *Chemical Process in Lakes*. Wiley, New York, pp. 251–281.
- Munawar, Muhammad Ehsan, 2018. Human health and environmental impacts of coal combustion and post-combustion wastes. *Journal of Sustainable Mining* 17 (2), 87–96.
- Muñiz-Unamunzaga, Maria, et al., 2018. The influence of ocean halogen and sulfur emissions in the air quality of a coastal megacity: the case of Los Angeles. *Sci. Total Environ.* 610, 1536–1545.
- Myhre, Gunnar, et al., 2013. Anthropogenic and natural radiative forcing. *Climate change* 423, 658–740.
- Myrriokefalitakis, Stelios, et al., 2015. Changes in dissolved iron deposition to the oceans driven by human activity: a 3-D global modelling study. *Biogeosciences* 12 (13), 3973–3992.
- Nakatani, Nobutake, et al., 2007. Contribution of the photo-Fenton reaction to hydroxyl radical formation rates in river and rain water samples. *Anal. Sci.* 23 (9), 1137–1142.

- O'Connor, Fiona, M., et al., 2010. Possible role of wetlands, permafrost, and methane hydrates in the methane cycle under future climate change: a review. *Rev. Geophys.* 48 (4).
- Observatory. Deep carbon, 2018 life in deep earth totals 15 to 23 billion tonnes of carbon—hundreds of times more than humans. <https://deepcarbon.net/life-deep-earth-totals-15-23-billion-tonnes-carbon>. (Accessed 10 February 2019).
- Oeste, F.D., et al., 2017. Climate engineering by mimicking the natural dust climate control: the Iron Salt Aerosols method. *Earth Syst. Dynam.* 8 (1), 1–54. <https://doi.org/10.5194/esd-8-1-2017>.
- Okin, Gregory S., et al., 2011. Impacts of atmospheric nutrient deposition on marine productivity: roles of nitrogen, phosphorus, and iron. *Global Biogeochem. Cycles* 25 (2).
- Paris, R., Desboeufs, K.V., 2013. Effect of atmospheric organic complexation on iron-bearing dust solubility. *Atmos. Chem. Phys.* 13 (9), 4895–4905.
- Pease, Camilla, Rücker, Thomas, Birk, Thomas, 2016. Review of the evidence from epidemiology, toxicology, and lung bioavailability on the carcinogenicity of inhaled iron oxide particulates. *Chem. Res. Toxicol.* 29 (3), 237–254.
- Pinedo-González, Paulina, et al., 2020. Anthropogenic asian aerosols provide Fe to the north pacific ocean. *Proc. Natl. Acad. Sci. Unit. States Am.* 117 (45), 27862–27868.
- Pires, J.C.M., 2019. Negative emissions technologies: a complementary solution for climate change mitigation. *Sci. Total Environ.* 672, 502–514.
- Pitchford, Jonathan William, Brindley, John, 1999. Iron limitation, grazing pressure and oceanic high nutrient-low chlorophyll(HNLC) regions. *J. Plankton Res.* 21 (3), 525–547.
- Pollard, Raymond T., et al., 2009. Southern Ocean deep-water carbon export enhanced by natural iron fertilization. *Nature* 457 (7229), 577–580.
- Proskurowski, Giora, et al., 2008. Abiogenic hydrocarbon production at Lost City hydrothermal field. *Science* 319 (5863), 604–607.
- Raiswell, R., et al., 2016. Potentially bioavailable iron delivery by iceberg-hosted sediments and atmospheric dust to the polar oceans. *Biogeosciences* 13 (13), 3887.
- Raju, M.P., et al., 2020. Black carbon aerosols over a high altitude station, Mahabaleshwar: radiative forcing and source apportionment. *Atmospheric Pollution Research* 11 (8), 1408–1417.
- Ramanathan, Veerabhadran, Carmichael, Gregory, 2008. Global and regional climate changes due to black carbon. *Nat. Geosci.* 1 (4), 221–227.
- Rathod, Sagar Dilipbhai, et al., 2020. A mineralogy-based anthropogenic combustion-iron emission inventory. *J. Geophys. Res.: Atmosphere* 125 (17), e2019JD032114.
- Ratnarajah, Lavenia, et al., 2017. Physical speciation and solubility of iron from baleen whale faecal material. *Mar. Chem.* 194, 79–88.
- Ratnarajah, Lavenia, et al., 2016. A preliminary model of iron fertilisation by baleen whales and Antarctic krill in the Southern Ocean: sensitivity of primary productivity estimates to parameter uncertainty. *Ecol. Model.* 320, 203–212.
- Ratnarajah, Lavenia, Nicol, Steve, Bowie, Andrew R., 2018. Pelagic iron recycling in the Southern Ocean: exploring the contribution of marine animals. *Frontiers in Marine Science* 5, 109.
- Raven, Morgan Reed, et al., 2018. Organic carbon burial during OAE2 driven by changes in the locus of organic matter sulfurization. *Nat. Commun.* 9 (1), 3409.
- Read, Katie A., et al., 2008. Extensive halogen-mediated ozone destruction over the tropical Atlantic Ocean. *Nature* 453 (7199), 1232–1235.
- Realmonte, Giulia, et al., 2019. An inter-model assessment of the role of direct air capture in deep mitigation pathways. *Nat. Commun.* 10 (1), 1–12.
- Rizzolo, Joana A., et al., 2017. Soluble iron nutrients in Saharan dust over the central Amazon rainforest. *Atmos. Chem. Phys.* 17 (4), 2673–2687.
- Robinson, J., et al., 2014. How deep is deep enough? Ocean iron fertilization and carbon sequestration in the Southern Ocean. *Geophys. Res. Lett.* 41 (7), 2489–2495.
- Roden, Eric E., Wetzel, Robert G., 1996. Organic carbon oxidation and suppression of methane production by microbial Fe (III) oxide reduction in vegetated and unvegetated freshwater wetland sediments. *Limnol. Oceanogr.* 41 (8), 1733–1748.
- Rojas-Valencia, Natalia, Jaime Gallego, Alexander, Santamaría, 2017. Effect of an iron compound added to diesel fuels in both soot reduction capacity and soot oxidation reactivity. *Energy Fuels* 31 (11), 12455–12465.
- Rombolà, Adamo D., Tagliavini, Massimo, 2006. Iron nutrition of fruit tree crops. In: *Iron Nutrition in Plants and Rhizospheric Microorganisms*. Springer, pp. 61–83.
- Roscoe, H.K., Kreher, K., Friess, U., 2001. Ozone loss episodes in the free Antarctic troposphere, suggesting a possible climate feedback. *Geophys. Res. Lett.* 28 (15), 2911–2914.
- Sabine, Christopher L., et al., 2004. The oceanic sink for anthropogenic CO₂. *science* 305 (5682), 367–371.
- Samsat, B.H., et al., 2018. Climate impacts from a removal of anthropogenic aerosol emissions. *Geophys. Res. Lett.* 45 (2), 1020–1029.
- Sarthou, Géraldine, et al., 2008. The fate of biogenic iron during a phytoplankton bloom induced by natural fertilisation: impact of copepod grazing. *Deep Sea Res. Part II Top. Stud. Oceanogr.* 55 (5–7), 734–751.
- Schmidt, Katrin, et al., 2011. Seabed foraging by Antarctic krill: implications for stock assessment, benthic-pelagic coupling, and the vertical transfer of iron. *Limnol. Oceanogr.* 56 (4), 1411–1428.
- Schmidt, Katrin, et al., 2016. Zooplankton gut passage mobilizes lithogenic iron for ocean productivity. *Curr. Biol.* 26 (19), 2667–2673.
- Seaton, Anthony, et al., 2005. The London Underground: dust and hazards to health. *JOEM (J. Occup. Environ. Med.)* 62 (6), 355–362.
- Sedwick, Peter N., Sholkovitz, Edward R., Church, Thomas M., 2007. Impact of anthropogenic combustion emissions on the fractional solubility of aerosol iron: evidence from the Sargasso Sea. *G-cubed* 8 (10).
- Shaffer, Gary, Lambert, Fabrice, 2018. And out of glacial extremes by way of dust—climate feedbacks. *Proc. Natl. Acad. Sci. Unit. States Am.* 115 (9), 2026–2031.
- Sherwen, Tomás, et al., 2016. Halogen chemistry reduces tropospheric O₃ radiative forcing. *Atmos. Chem. Phys. Discuss.* 10.
- Shi, Zongbo, et al., 2009. Formation of iron nanoparticles and increase in iron reactivity in mineral dust during simulated cloud processing. *Environ. Sci. Technol.* 43 (17), 6592–6596.
- Shi, Zongbo, et al., 2015. Atmospheric processing outside clouds increases soluble iron in mineral dust. *Environ. Sci. Technol.* 49 (3), 1472–1477.
- Shilobreeva, S., et al., 2011. Insights into C and H storage in the altered oceanic crust: results from ODP/IODP Hole 1256D. *Geochem. Cosmochim. Acta* 75 (9), 2237–2255.
- Shindell, Drew, et al., 2012. Simultaneously mitigating near-term climate change and improving human health and food security. *Science* 335 (6065), 183–189.
- Shoenfelt, Elizabeth M., et al., 2018. Highly bioavailable dust-borne iron delivered to the Southern Ocean during glacial periods. *Proc. Natl. Acad. Sci. Unit. States Am.* 115 (44), 11180–11185.
- Sigman, Daniel M., Hain, Mathis P., Haug, Gerald H., 2010. The polar ocean and glacial cycles in atmospheric CO₂ concentration. *Nature* 466 (7302), 47–55.
- Sivan, O., Shusta, S.S., Valentine, D.L., 2016. Methanogens rapidly transition from methane production to iron reduction. *Geobiology* 14 (2), 190–203.
- Sivan, Orit, et al., 2014. Iron oxides stimulate sulfate-driven anaerobic methane oxidation in seeps. *Proc. Natl. Acad. Sci. Unit. States Am.* 111 (40), E4139–E4147.
- Six, Katharina D., et al., 2013. Global warming amplified by reduced sulphur fluxes as a result of ocean acidification. *Nat. Clim. Change* 3 (11), 975–978.
- Smayda, Theodore J., 1971. Normal and accelerated sinking of phytoplankton in the sea. *Mar. Geol.* 11 (2), 105–122.
- Smetacek, Victor, 2018. Seeing is believing: diatoms and the ocean carbon cycle revisited. *Protist* 169 (6), 791–802.
- Smetacek, Victor, et al., 2012. Deep carbon export from a Southern Ocean iron-fertilized diatom bloom. *Nature* 487 (7407), 313–319.
- Smith, J.D., et al., 2020. PM_{2.5} on the london underground. *J Environment international* 134, 105188.
- Sofiev, Mikhail, et al., 2018. Cleaner fuels for ships provide public health benefits with climate tradeoffs. *Nat. Commun.* 9 (1), 406.
- Sommariva, Roberto, von Glasow, Roland, 2012. Multiphase halogen chemistry in the tropical Atlantic Ocean. *Environ. Sci. Technol.* 46 (19), 10429–10437.
- Srinivas, Bikkina, Sarin, M.M., Rengarajan, R., 2014. Atmospheric transport of mineral dust from the Indo-Gangetic Plain: temporal variability, acid processing, and iron solubility. *G-cubed* 15 (8), 3226–3243.
- Stoll, Heather, 2020. 30 years of the iron hypothesis of ice ages. *Nature* 370–371.
- Struve, Torben, et al., 2020. A circumpolar dust conveyor in the glacial Southern Ocean. *Nat. Commun.* 11 (1), 1–11.
- Stukel, Michael R., et al., 2018. The role of subduction and gravitational sinking in particle export, carbon sequestration, and the remineralization length scale in the California Current Ecosystem. *Limnol. Oceanogr.* 63 (1), 363–383.
- Sunda, William G., Swift, Dorothy G., Huntsman, Susan A., 1991. Low iron requirement for growth in oceanic phytoplankton. *Nature* 351 (6321), 55.
- Sur, Sohini, et al., 2015. Extreme eolian delivery of reactive iron to late Paleozoic icehouse seas. *Geology* 43 (12), 1099–1102.
- Taalab, A.S., et al., 2019. Some characteristics of calcareous soils. A review. *Middle East Journal of Agriculture Research* 8 (1), 96–105.
- Tang, Lan, et al., 2019. Experimental study on high frequency capacitively coupled plasma-catalysis hybrid system for methane complete oxidation. *Atmospheric Pollution Research* 10 (1), 24–29.
- Tarling, Geraint A., Thorpe, Sally E., 2017. Oceanic swarms of Antarctic krill perform satiation sinking. *Proc. R. Soc. B* 284 (1869), 20172015.
- Thamdrup, Bo, Schubert, Carsten J., 2013. Anaerobic oxidation of methane in an iron-rich Danish freshwater lake sediment. *Limnol. Oceanogr.* 58 (2), 546–554.
- Thomas, Jennie L., et al., 2006. Gas-phase molecular halogen formation from NaCl and NaBr aerosols: when are interface reactions important? *J. Phys. Chem.* 110 (5), 1859–1867.
- Thornton, Joel A., et al., 2010. A large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry. *Nature* 464 (7286), 271.
- Trommer, Gabriele, et al., 2012. Zooplankton-mediated nutrient limitation patterns in marine phytoplankton: an experimental approach with natural communities. *Mar. Ecol. Prog. Ser.* 449, 83–94.
- Turner, Jefferson T., 2015. Zooplankton fecal pellets, marine snow, phytodetritus and the ocean's biological pump. *Prog. Oceanogr.* 130, 205–248.
- Twining, Benjamin S., et al., 2004. Cellular iron contents of plankton during the Southern Ocean iron experiment (SOFEX). *Deep Sea Res. Oceanogr. Res. Pap.* 51 (12), 1827–1850.
- Valdes, Paul J., Beerling, David J., Johnson, Colin E., 2005. The ice age methane budget. *Geophys. Res. Lett.* 32 (2).
- Wang, Rong, et al., 2015a. Influence of anthropogenic aerosol deposition on the relationship between oceanic productivity and warming. *Geophys. Res. Lett.* 42 (24).
- Wang, Rong, et al., 2015b. Sources, transport and deposition of iron in the global atmosphere. *Atmos. Chem. Phys.* 15 (11), 6247–6270.
- Wang, Rong, et al., 2015c. Significant contribution of combustion-related emissions to the atmospheric phosphorus budget. *Nat. Geosci.* 8 (1), 48.
- Wang, Weiqi, et al., 2014. Steel slag amendment reduces methane emission and increases rice productivity in subtropical paddy fields in China. *Wetl. Ecol. Manag.* 22 (6), 683–691.
- Wang, Xuan, et al., 2019. The role of chlorine in global tropospheric chemistry. *Atmos. Chem. Phys.* 19 (6), 3981–4003.
- Watson, Andrew J., James, E Lovelock, 1983. Biological homeostasis of the global environment: the parable of Daisyworld. *Tellus B* 35 (4), 284–289.

- Wikipedia, 2018. List of Gasoline Additives. https://en.wikipedia.org/wiki/List_of_gasoline_additives. (Accessed 10 February 2019).
- Williamson, Phillip, et al., 2012. Ocean fertilization for geoengineering: a review of effectiveness, environmental impacts and emerging governance. *Process Saf. Environ. Protect.* 90 (6), 475–488.
- Wing, S.R., et al., 2017. ^{85}Fe in seabird guano reveals extensive recycling of iron in the Southern Ocean ecosystem. *Limnol. Oceanogr.* 62 (4), 1671–1681.
- Wing, S.R., et al., 2014. Seabirds and marine mammals redistribute bioavailable iron in the Southern Ocean. *Mar. Ecol. Prog. Ser.* 510, 1–13.
- Wingenter, Oliver W., 2007. New Directions: enhancing the natural sulfur cycle to slow global warming. *Atmos. Environ.* 41, 7373–7375.
- Wingenter, Oliver W., Scott, M Elliot, Blake, Donald R., 2007. New Directions: enhancing the natural sulfur cycle to slow global warming. *Atmos. Environ.* 41 (34), 7373–7375.
- Wittmer, J., Bleicher, S., Zetzsch, C., 2016. Report on the photochemical induced halogen activation of Fe-containing aerosols. *J. Climatol Weather Forecasting* 4 (169), 2.
- Wittmer, Julian, et al., 2015a. Iron (III)-induced activation of chloride from artificial sea-salt aerosol. *Environ. Chem.* 12 (4), 461–475.
- Wittmer, Julian, Bleicher, Sergej, Zetzsch, Cornelius, 2015b. Iron (III)-induced activation of chloride and bromide from modeled salt pans. *J. Phys. Chem.* 119 (19), 4373–4385.
- Wittmer, Julian, Zetzsch, Cornelius, 2016. Photochemical activation of chlorine by iron-oxide aerosol. *J. Atmos. Chem.* <https://doi.org/10.1007/s10874-016-9336-6>:1–18.
- Wittmer, Julian, Zetzsch, Cornelius, 2017. Photochemical activation of chlorine by iron-oxide aerosol. *J. Atmos. Chem.* 74 (2), 187–204.
- Wu, Wei, et al., 2015. Recent progress on magnetic iron oxide nanoparticles: synthesis, surface functional strategies and biomedical applications. *Sci. Technol. Adv. Mater.* 16 (2), 023501.
- Yoon, Joo-Eun, et al., 2018. Reviews and syntheses: ocean iron fertilization experiments—past, present, and future looking to a future Korean Iron Fertilization Experiment in the Southern Ocean (KIFES) project. *Biogeosciences* 15 (19), 5847–5889.
- Yu, Hongbin, et al., 2015. The fertilizing role of African dust in the Amazon rainforest: a first multiyear assessment based on data from Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observations. *Geophys. Res. Lett.* 42 (6), 1984–1991.
- Zetzsch, C., Bleicher, S., Wittmer, J., 2013. Smog chamber investigation on the iron-catalyzed activation of chloride from seasalt for a depletion of tropospheric methane. In: *AGU Fall Meeting Abstracts A13D-0229*, vol. 2013, 2013.
- Zhang, Chuanlun, et al., 2018. Evolving paradigms in biological carbon cycling in the ocean. *National Science Review* 5 (4), 481–499.
- Zhang, Dongke, et al., 2009. Homogeneous Combustion Catalysts for Efficiency Improvements and Emission Reduction in Diesel Engines. *Handbook of Clean Energy Systems*.
- Zhang, Yingchao, et al., 2017. Role of ferric oxide in abiotic humification enhancement of organic matter. *J. Mater. Cycles Waste Manag.* 19 (1), 585–591.
- Zhou, Linbin, et al., 2018. Aluminum effects on marine phytoplankton: implications for a revised iron hypothesis (Iron–Aluminum hypothesis). *Biogeochemistry* 139 (2), 123–137.