

Deserts: Can they be the potential suppliers of bioavailable iron?

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[1] The temporal and spatial variability of bioavailable iron delivered to the ocean may be controlled via in-cloud photochemical reduction of desert dust, assisted by the impact of oxalate released by fungi in the desert soil. The basic process in the photochemical production of bioavailable iron through decarboxylation reaction involves simultaneous action of oxalate released by the fungus encapsulated in a cloud droplet, above some threshold solar radiation. Therefore, diurnal and latitudinal variations in solar irradiation and the sporadic nature of rain along the path of the synoptic-scale atmospheric depressions are the governing factors that determine spatial and temporal distribution of phytoplankton growth and especially that of coccolithophorid blooms on the ocean surface. **INDEX TERMS:** 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 4807 Oceanography: Biological and Chemical: Chemical speciation and complexation

1. Introduction

[2] The experimental demonstration of iron's role in the regulation of key biogeochemical interactions between the ocean and atmosphere, and the availability of SeaWiFS satellite data have drawn our attention to dust transport mechanisms, with the recognition that a primary transport vehicle for iron found in the ocean is atmospheric dust [Boyd *et al.*, 2000]. Still, the limiting role of iron for many classes of pelagic organisms is not easily acceptable since iron is one of the most abundant elements in the earth's crust and the total infusion of iron to the oceans from the atmosphere has been estimated to be 15–100 Tg yr⁻¹. However, iron limitation is often related to its uneven distribution with the lowest deposition measured in remote ocean regions, as well as its low solubility and a mineralogical composition that is not readily usable by the primary producers. Zhuang *et al.* [1992] suggested that a Aeolian dust may be trapped within acidic sulfate cloud droplets and can be converted to relatively soluble ferrous ion through photochemical reduction, thereby increasing the bioavailability of iron. A feedback loop has also been proposed between the atmospheric and oceanic iron and sulfur cycles, based on DMS emissions driven by acid Cloud Condensation Nuclei (CCN) formation, iron dissolution and ensuing input of bio-available iron to the oceans, which in turn stimulate phytoplankton productivity and hence emissions of DMS, to complete the loop. Links between oceanic blooms of DMSP-synthesizing micro-algae, DMS flux to the atmosphere and cloud formation are well established. Despite this, however, the unexpected appearance of these blooms is still not fully understood [Hegg *et al.*, 1991]. The analyses of the DMS proxy MSA and non-sea salt sulfate in Antarctic ice cores have further demonstrated increased atmospheric DMS concentrations

during the last glaciation [Legrand *et al.*, 1991], and this is suggested to coincide with enhanced levels of primary productivity and iron inputs to the Southern Ocean [Kumar *et al.*, 1995]. Recently it was shown that the load of aerosol in the Last Glacial Maximum atmosphere over Greenland and east Antarctica was higher by a factor of about 90–125 compared to the pre-industrial interglacial atmosphere. The three major potential sources of dust in the Southern Hemisphere are Patagonia, Australia and South Africa [Lunt and Valdes, 2001]. Moreover, Griffin *et al.* [2001] have shown that the samples collected at St. John at US Virgin Island during "African dust-events," have 2 to 3 times more cultivatable airborne microorganisms and one log greater bacteria-like particles, than those found during "clear atmospheric conditions". Sulzberger and Laubscher [1995] have shown the light-induced dissolution and photochemical production of Fe(II) by using lepidocrocite and oxalate as a reductant based on the assumption that oxalate is present in atmospheric waters due to anthropogenic sources. Here we suggest that desert soil is a potential source of bioavailable iron through in-cloud photochemical reduction of iron minerals assisted by the oxalate released by fungi present within the desert soil.

2. Experiments and Results

[3] The first step of our experimental approach was to illustrate the possible formation of oxalate as reductant by using the Saharan desert soil sample. For this purpose, 10 g of dry, sieved (30 μ mesh), homogenized soil samples imported from Sahara were mixed with 500 ml of distilled deionized water and irradiated with 1500-Watt tungsten light with a wavelength spectrum of 380–800 nm, at constant ambient temperature, so as to simulate the encapsulated dust within a cloud droplet during the day time. The ion chromatographic analysis of the aliquot taken after 120 minutes has confirmed the presence of reducing agent, oxalate, together with sulfate and phosphate within the mixture as illustrated in Figure 1.

[4] The acidic nature of an oxalate allows fungi to attach to the mineral lattice during long-range atmospheric transport and to form iron oxalate complexes with various iron minerals present in the dust. The formation of bioavailable iron necessitates the presence of a light source to induce decarboxylation reactions as suggested by Sulzberger and Laubscher [1995]. The diurnal cycle of solar light may supply the necessary energy, provided that solar energy is above some threshold level that varies latitudinally and seasonally. To test the possible formation of Fe(II), we designed a reaction vessel in which it was possible to keep the entire system at constant temperature by circulating ice water while irradiating it with a (3 \times 500)-Watt tungsten light with a wavelength spectrum of 380–800 nm. The experiments used 500 ml of distilled deionized water mixed with 10 g of dry, sieved (30 μ mesh), homogenized soil samples imported from the northern Sahara (south Tunisia), Saudi Arabia (near Riyadh) and various, supposedly fertile soil samples from Turkey. The pH of the solution was adjusted so as to be 2–3 throughout the experiment. Samples taken at the start and at various stages of irradiation were immediately analyzed by Post Column Derivatization- HPLC, equipped with the following: IonPac CS5A and CG5A guard; MetPac PDCA eluent and PAR for derivatization with 1.2 ml/min flow rate at 521 nm UV-Vis detector for analysis of cations. The results showed that,

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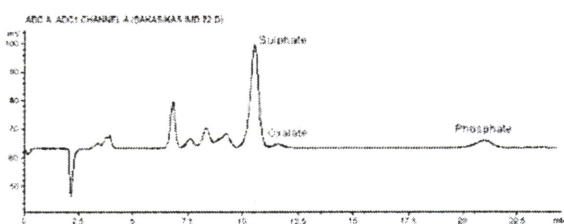


Figure 1. The chromatogram of sulphate, oxalate and phosphate in irradiated Sahara desert dust sample in 100 μ l injection volume. Column: AS15 anion column, 250 \times 4 mm I.D.; eluent 40 mM NaOH, flow rate; 1.2 ml/min, detection conductivity.

during irradiation, it is possible to observe the photochemical formation of Fe(II) and the release of some other essential micro-nutrient elements like Zn(II) and Mn(II), likely originating from the decomposition of minerals following the photochemical release of iron as illustrated in Figure 2. The photochemical formation of Fe(II) reached a steady state within 120 minutes. To illustrate the effect of light on the formation of Fe(II), irradiation was terminated at the 210th minute and the entire system was kept in darkness. A gradual decrease in the Fe(II) concentration was observed after two hours, possibly due to the oxidation of Fe(II) to its stable form of Fe(III). The variations in Zn and Mn are not discussed here, but it is important to illustrate their existence in the system together with PO₄, since they support the view that desert soil has the potential of supplying some essential micronutrient elements.

[5] Similar experiments were conducted with various other soil samples under identical laboratory conditions. Here, we further demonstrate that the photochemical production of Fe(II) is limited to soil samples obtained from the northern Sahara, whereas soil samples obtained from the Arabian Desert resulted in an order of magnitude less Fe(II) production and reputedly fertile soil samples taken from different locations in Turkey yielded practically no Fe(II) at all, as illustrated in Figure 3.

[6] To illustrate the possible effect of fungal activity on the photochemical production of Fe(II), various non-destructive sterilization methods were tested with the Saharan soil samples, since any wet sterilization with chemicals precludes the application of

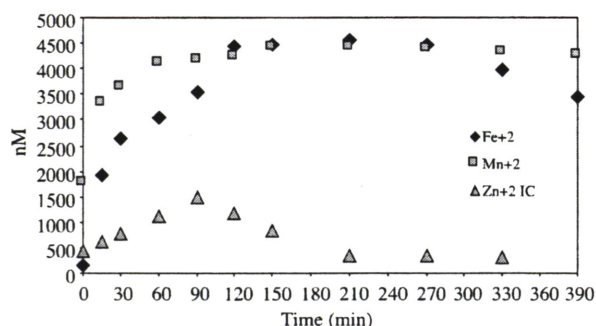


Figure 2. The photochemical formation of Fe(II), and the production of Mn(II) and Zn(II) at pH 2–3 at constant temperature by using 10 g of Sahara soil sample dry sieved through 30 μ mesh in 500 ml deionised water Post Column Derivatization- HPLC equipped with: IonPac CS5A and CG5A guard; MetPac PDCA eluent and PAR for derivatization with 1.2 ml/min flow rate at 521 nm UV-Vis. detector for analysis of cations. 3 \times 500 Watt tungsten lights were used for irradiation for 210 minutes and the reaction vessel kept at constant temperature by circulating ice water. Irradiation terminated at 210 min and the entire system kept in darkness at constant temperature.

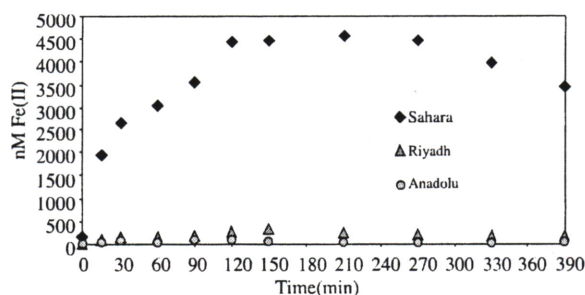


Figure 3. The photochemical production of Fe(II) by using different samples from various geographic regions. 10 g of soil samples taken from each sample and dry sieved through 30 μ mesh and diluted to 500 ml with deionised water. 3 \times 500 Watt tungsten lights were used for irradiation up to 210 minutes, and the reaction vessel kept at constant temperature by circulating ice water. Irradiation was terminated at 210th minute and the entire system was kept in darkness.

chromatography and may alter the original composition of the samples. We observed a gradual decrease in the photochemical formation of Fe(II) following 1000-Watt microwave oven treatment. After irradiation with low intensity Co⁶⁰ gamma rays, there was no increase in Fe(II) apart from what was measured initially at pH range 2–3. This confirms the essential role of the fungal action in the overall cation production mechanism.

[7] Similar irradiation experiments were repeated by wetting the same amount of soil sample with seawater collected from surface of the eastern Mediterranean with a salinity of 38.5 ppt, and no HPLC detectable initial Fe(II) concentrations. The irradiation experiment did not produce any cations, suggesting the possible inhibition of fungal activity by salt water or the inability of fungi to bind to mineral surfaces due to dilution effects. This result may explain why dry dust deposition over the oceans does not always yield phytoplankton blooms, even if the dust pulses originate from the Sahara.

[8] Daytime, rainwater sampling in Ankara during the course of the Sahara dust transport event of 12 May 2000 confirmed the presence of the cations Fe(II), Zn(II) and Mn(II). The sample collected during the night of a wet dust deposition event on 6 June 2000 did not display any of the above mentioned ions; but upon irradiation at laboratory conditions, the production of Fe(II), and the release of Zn(II) and Mn(II) were detected instrumentally, confirming the essential role of photochemistry as a cation production mechanism. At this point, we cannot explain why we did not observe Zn and Mn in the sample collected during the night of 6 June 2000, but as mentioned before, our aim at this stage is demonstration of their presence rather than the discussion of their variations.

3. Conclusions and Recommendations

[9] Following the results of iron addition experiments, the scientific community now accepts that iron delivery has the potential to change the absolute level of primary productivity and the structure of the pelagic food chain that added iron results in reduced CO₂ levels, and that certain kinds of phytoplankton, such as coccolithophorids, can be enhanced. All seeding experiments utilized iron in the form of Fe(II). Here, we were able to show that dust from specific deserts has the potential to produce bioavailable iron within cloud droplets and that daytime wet dust deposition over the ocean surface results in the enhancement of coccolithophores as mentioned in *Guerzoni et al.* [1999].

[10] Following the results of this work, we now have the potential of seeding the clouds with a natural ingredient, desert

soil, and enhance the photochemical formation of iron as well as producing some other essential nutrient elements like Mn and Zn along with PO₄. Our experimental results showed that after the light was switched off, the Fe(II) concentrations had dropped noticeably after two hours. In nature, this transformation takes place within hours and complex atmospheric systems may further enhance the lifetime of Fe(II), a possibility which should be studied in more detail.

[11] This work also carries great potential as it may pave the way for comprehensive studies on the properties of desert soil, – i.e., Sahara, Central Asian and Gobi in the northern hemisphere and Patagonian, Australian and Namibian deserts in the south – with this novel perspective.

[12] This work carries even more importance for those developing nations that happen to own such resources, which were so far dismissed as useless land. Our work offers them the prospect of prosperity, since now we have the technology to be at the right place at right time of the day “to seed the clouds” with the correct composition of desert dust to sustain phytoplankton growth over the oceans, possibly with a stabilizing effect on climate, as suggested by Charlson *et al.* [1987].

[13] **Acknowledgments.** We are grateful to Merit Shipping and Trading Ltd. Izmir/Turkey for their financial support.

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