IJEGEO International Journal of Environment and Geoinformatics 1(1-3), 1-11 (2014)

Desert Dust Cloud Interactions and Natural Iron Enrichment Mechanism

A. Cemal Saydam [1*]

[1]Hacettepe University, Department of Environmental Engineering, 06800, BEYTEPE, ANKARA-TR

Corresponding author. Tel: +90 312 2977168
E-mail: acsaydam@gmail.com

Received 20 July 2014
Accepted 30 Sept. 2014

Abstract

Iron enrichment hypothesis have been tested on many occasions by adding dissolved iron into the seawater. Though Mediterranean Sea never depleted with iron it is one of the most oligotrophic water that exists on earth. It's shown that oceanic surface chlorophyll levels do in fact regulated by the wet desert dust deposition, independent of the nutritional load of the receiving body. The in cloud alteration of desert dust matrix and its biological content is in fact responsible from the reaction mechanisms initiated via the oxalate released by the prokaryotes. Solar light further enhances the formation of dissolved iron via decarboxylation reaction. Thus this paper explains the pathways of natural iron fertilization mechanisms that can be regulated by seeding the clouds with appropriate desert dust hence offers a means to control the chlorophyll concentration hence control on the negative feedback mechanisms on climate.

Keywords: Dust, prokaryote, cloud, oxalate, solar intensity, decarboxylation, reduced iron, algae.

Introduction

Transport of desert dust is a well-known and well-documented process and often gives spectacular images via existing satellites. Sahara being the largest desert on globe emanates dust on various directions and MODIS satellites documents its local and intercontinental transport via trade winds as illustrated in July 31st 2013, satellite image shown in Figure 1. Gobi and Taklimakan deserts on the other hand supplies large amounts of dust towards North Pacific Ocean and beyond. US and Mexican deserts further contributes to the dust burden on the Northern Hemisphere. In general, the perennial dust sources from a series of ephemeral/dry lakes contribute to atmospheric dust burden along with the wind's that is associated with synoptic scale meteorological events on both hemispheres. All these migration patterns are clearly traced by recent MODIS Terra or Aqua satellites and near real time data can also be reached at respective sites available through the Internet. Of course sporadic unexpected dust sources can also be traced via satellites such as dust from losses at Alaska Glaciers or from some unexpected arid lands such as Washington State at USA.Southern hemisphere also possesses desert regions though much less compared to northern hemisphere. Patagonia and Bolivian deserts on Southern American continent, Namibian desert on Southern Africa and Great Australian desert further contributes to dust burden of the Southern Hemisphere. Toon (2003) reports on the subject of African dust in Florida clouds, covers many aspects of the impact of dust on natural systems. (Charlson et al.,1987; Jickells et al., 2005) considered the important part of this transport in which iron containing soil dust affecting ocean biogeochemistry and hence having feedback effects on climate. But all these arguments based on the assumption that iron content of the soil dust somehow dissolved in seawater since this form of iron is necessary for the growth of phytoplankton. Baker and Croot (2010) have shown the importance of this process but also mentioned our poor understanding of the iron dissolution within seawater. The picture can be more comprehensive if so far neglected part of the dust i.e., microorganisms are embedded into the story.

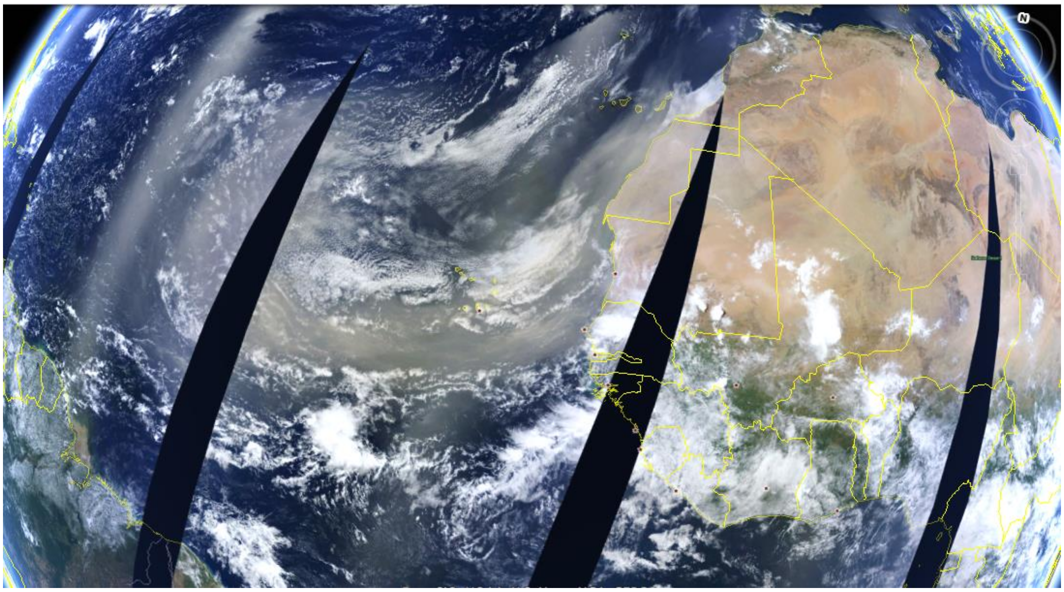


Fig 1. The transport of Sharan dust across Atlantic Ocean via trade winds. This image is captured by MODIS satellites on 31st July 2013.

It has been shown that (Smith et al., 2013; Kellogg and Griffin, 2006; Griffin et al., 2001; Griffin et al., 2007) Asian and Saharan dust plumes may serve not only as a periodic source of nutrients for terrestrial plants and primary producers in nutrient depleted oceanic waters, but may also serve as a medium for the global transport of microorganisms as microbes are being transported from Africa and Asia via dust flux to the Caribbean and the America.

Scientific community so far either concentrated on the dry dust transport since it's easy to eliminate clouds due their strong reflectance or focused on the microbial composition and totally ignored the state where dust and cloud water comes into contact. This so far neglected part is also understandable since at present it's impossible to detect desert dust cloud interactions via existing sensors on board various satellites.

Saydam and Senyuva (2002) simply combined these two states ie., desert dust matrix and cloud water and highlighted the interactions and the resulting reaction products of these two component for the first time in scientific history. The author further postulates that, low pressure systems and associated warm and cold fronts that are responsible from the uplift and transport of desert dust are designed to act as a conveyor belt for the transport of dust having 10 micron or less in size. During the course of such transport mechanism desert dust is segregated from its large fractions, less than 10 micron size fraction is uplifted with the help of winds associated with warm frontal system and. The downward action of cold front further helps and uplifts the entire warm front so that the associated dust particles can reach to their maximum elevations. The author assumes that this natural phenomenon is designed to enhance the desert dust cloud mixtures as shown in Figure 2.

One of the most essential discoveries made by (Saydam and Senyuva, 2002) lies in the fact that oxalate, the most abundant dicarboxylic acid in atmosphere is in fact generated by the biological component of the desert dust upon contact with cloud water. Though the impact of oxalic acid in the chemical weathering of rocks by the excretion of various organic acids, particularly oxalic acid, which can effectively dissolve minerals and chelate metallic cations is a known process (Chen et al., 2000) up to date no one assumed that similar mechanisms can also be effective within the clouds.

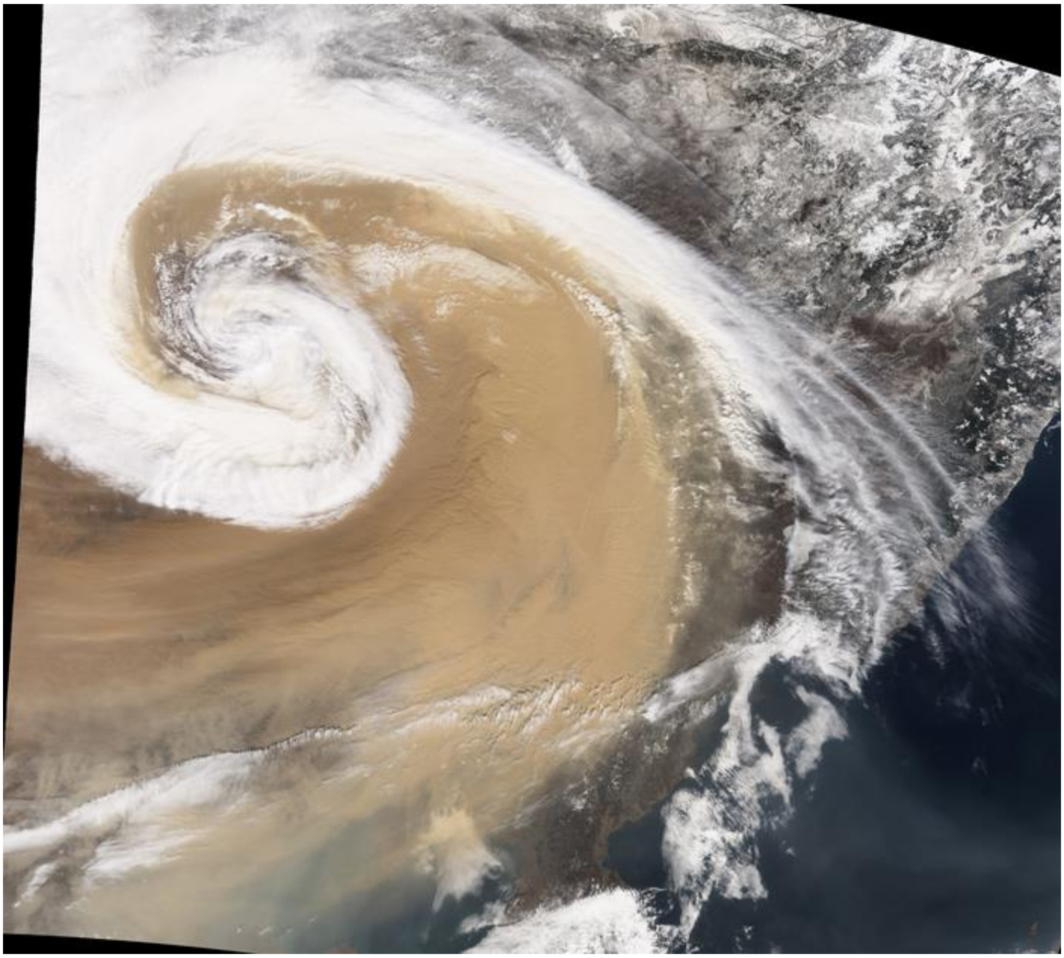


Figure 2. Cyclonic activity and associated dust and cloud migration patterns over the Gobi desert on April 7th 2001. It should be noted that warm front raises and cold front sinks the air mass and associated particles in it. Cold front sweeps through the snow covered or thawed land parcels, while warm front transports and uplifts 10 micron and less particle size clay minerals. Thus if we think this motion in three dimension we can see that synoptic scale meteorological events acts as a mere cloud seeding mechanism by desert dust.

It is known that each gram of soil can accommodate prokaryotes that vary between 10^{7-12} in number (Leininger et al., 2006). As dry these prokaryotes keep their identity for indefinite time span but once came into contact with cloud water they become active and releases oxalate as an osmosolute within minutes. Such combination can take place via the action of cyclonic activities over the desert regions as shown in Figure 2. The author named this phenomena as “cloud dusting” analogues to soil irrigation. Fungi’s associated oxalate production mechanism is so effective that *Aspergillus niger* is still used in the production of industrial scale oxalic acid (Ruijter et al.,1999). On the other hand oxalic acid, globally the most abundant atmospheric dicarboxylic acid, still assumed to be formed via chemical oxidation of gas phase precursors in the aqueous phase of aerosols and droplets (Myriokefalitakis., 2011). Sorooshian et al.,(2006) supports these in cloud production mechanisms as they observe very strong correlation between oxalate and SO_4. Levin et al.,(1996) also reported the presence of sulfate in the eastern Mediterranean aerosol particles. But sulfate also assumed to be formed entirely by industrial activities. Yu et al. (2005) also highlighted the importance of oxalic acid but also mentioned that its precursors have not been identified, and its formation mechanism is not well understood. On the contrary, sulfate as a major aerosol component, its formation pathways have been established, and in-cloud processing is recognized as its major production pathway.

As mentioned by (Sorooshian et al., 2006) measurements also indicates that the two species are highly correlated among samples collected at the same location just like measurements made elsewhere by other researchers. This also highlights the potential importance of in-cloud processing as a pathway leading to formation of secondary organic aerosols.

This so far unexplained source of oxalate is in fact produced within the cloud droplets by the cellular activities of the prokaryotes that are embedded in desert origin dust. Saydam and Senyuva (2002) have confirmed this essential in cloud activity of the desert dust matrix since gamma irradiated desert dust matrix in other word following complete sterilization ceased oxalate production confirming the vital role of prokaryotes.

During the course of the atmospheric transport of desert dust upon contact with cloud water the release of oxalate by the prokaryotes is followed by the formation of iron oxalate (R1).

$\Xi\ \mathrm{FeOH} + \mathrm{HC_2O^-_4} \longrightarrow \mathrm{FeC_2O^-_4} + \mathrm{H_2O}$ (R1)
Ξ FeOH represents the surface lattice of an Fe(III) (hydr)oxide

It should be remembered that dust and cloud combination takes place within a synoptic scale meteorological event and the system is in constant migration pattern that shifts towards north or south due to coriolis effect and this migration pattern also affects the solar radiation intensity that also varies latitudinally.

If the solar radiation is above some threshold level along the path of the synoptic scale ($\cong$200 Watt m^{-2}) atmospheric depression, photochemical production of bioavailable iron Fe^{+2} takes place as a result of decarboxylation reaction (R2).

$\mathrm{FeC_2O^-_4} \longrightarrow \mathrm{Fe^{+2}} + \mathrm{CO_2} + \mathrm{CO_2}$ (R2)

The production of reduced iron ($Fe^{+2)}$ is very important since this is the form of iron can be utilized by the organisms. It is known that the availability of iron limits primary productivity and plays an important role in the carbon cycle, and changes in its supply to the surface ocean may have had a significant effect on atmospheric carbon dioxide concentrations over glacial–interglacial cycles. Due to this fact the impact of iron in carbon cycling has been assessed using short-term iron-addition experiments and that’s why, iron sulfate ($FeSO_4$) is used as seeding chemical along with various tracers as to test the Martin’s (1992) iron hypothesis. In other words in cloud alterations of the desert dust explains the natural iron fertilization mechanism that is so far not yet discovered by the scientific community.

It has been further shown that upon irradiation by using desert dust imported from Sahara/Southern Tunisia sulfate production increased indefinitely. This rather surprising result have been obtained by running parallel soil samples collected from various other places as shown in Figure 3. Thus Saharan desert dust possesses this unique property that upon irradiation sulfate production is also increased. This may explain the reason why oxalate and sulfate is found together within the clouds and also shows our misunderstanding since we all accept sulfate as an indicator of acidity.

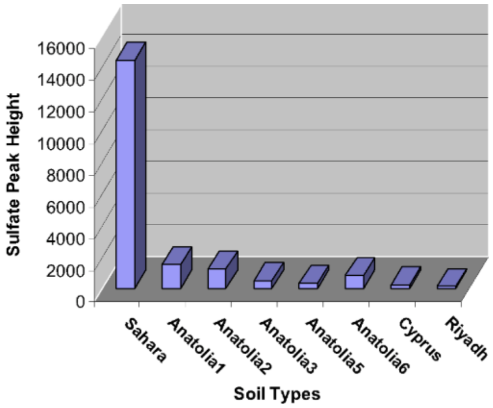


Fig 3. Sulfate production capacities of various irradiated soil samples. It can be seen that Saharan sample do generate sulfate much more than any other soil sample upon irradiation.

In addition to Fe^{+2}, as a result of decarboxylation reaction one mole of carbon dioxide and carbonyl radical also released into the atmosphere, offering us, so far unrealized, but significant natural source of atmospheric carbon dioxide (Hadjialighandi;2011). Thus the temporal and spatial variability of bioavailable iron as well as other micronutrient elements such as Zn and Mn can be produced within the clouds and regulated by the latitudinal variations in solar irradiation along the path of the synoptic-scale atmospheric depression (Saydam and Senyuva, 2002). It has been further shown by (Mace et al.,2004) that rain events originating from Sahara further enhanced by various amino acids. Thus the temporal and spatial variability of bioavailable iron as well as other micronutrient elements such as Zn and Mn and amino acids delivered to the oceans is controlled by the diurnal and latitudinal variations in solar irradiation and the sporadic nature of rain along the path of the synoptic-scale atmospheric depressions.

In cloud reaction mechanisms do possess feedback mechanisms since carbonyl radical is reductant and reacts either with O_2 (R3) resulting with one mole of CO2 or with another surface (R4) resulting with one mole of CO2 and reduced ion or dissolved Fe(III) resulting with one mole of CO2 and soluble iron species (R5) or may combine with another one (R6) and result with one more oxalate molecule as to initiate yet another reaction cycle.

$CO^{-}_2 + O_2 \longrightarrow CO_2 + O^{-}_2$ (R3)
$CO^{-}_2 + \Xi\ FeOH \longrightarrow CO2 + \Xi\ Fe(II)$ (R4)
$CO^{-}_2 + Fe(III) \longrightarrow CO2 + Fe(II)_{aq}$ (R5)
$CO^{-}_2 + CO^{-}2 \longrightarrow C2O4$ (R6)

It should be noted that one of the end products of the decarboxylation reaction (R2) as well as (R3-4 and5) are CO_2. The pH of wet dust depositions originated from Sahara also varies between 5.78-7.97 (Guieu et al,2002 and references therein) and at this pH CO_2 shifts entirely to bicarbonate. In other words carbon dioxide turns into a form of carbon that is readily available for the utilization by living organisms either within the clouds or at ground level. Rogora et al.,(2004) has shown that Saharan events, despite their small contribution to total annual precipitation (3–17%), carry a considerable fraction of the annual total calcium and bicarbonate deposition (up to 70 and 100% respectively) over Italy.

Thus, as a result of desert dust cloud interactions the associated rain events enhances the receiving body with dissolved iron, amino acids and various natural fertilizers that is necessary to enhance phytoplankton bloom or high concentrations. In fact this has been hypothesized by Saydam and named as Cemiliania Hypothesis (Guerzoni et al.,1996)
In this paper we will concentrate on the impact of wet dust deposition over the Mediterranean Sea by using data available thorough Internet and through Giovanni interactive visualization and analysis. Mediterranean offers an ideal place as to test the impact of wet dust deposition on the formation of chlorophyll bloom due to its oligotrophic nature especially at the eastern basin.

Results and Discussion

If we have a look at the annual variations at dust deposition as Aeresol Optical Depth (Figure 4) its possible to observe general increasing trends during the course of winter/spring seasons. Precipitation (Figure 5) also follows similar pattern having significantly low levels during hot summer and early autumn seasons. Surprisingly overall chlorophyll levels (Figure 6) also resemble AOD and precipitation levels. Even though such general picture suggest a possible correlation amongst chlorophyll, precipitation and dust it’s not easy to make a generalization. On the other hand we do also know that dust pulses are sporadic in nature and each one has a unique precipitation patterns over the basin. Thus we have investigated specific dust pulse and its possible impact on the receiving body.

On 13 March 2014, cyclonic depression (Figure 7) was developed over the Northern Sahara with 1006 hPa pressure. In association with this depression dust and cloud covered off the coast of Algeria as shown in Figure 8. On 14th March 2014 the cyclonic activity was still active over the Mediterranean Sea as shown in Figure 9.
The rain pattern in association with this depression during the course of 13 and 14 March 2014 as captured by TRMM satellite is

shown on Figure 10. The rain pattern can also be traced on an hourly basis as sown in Figure 11. It can be seen that from 14-15 GMT while the solar light intensity is at its maximum the rain pattern extends as shown in Figure 11, far way from any local riverine influx.

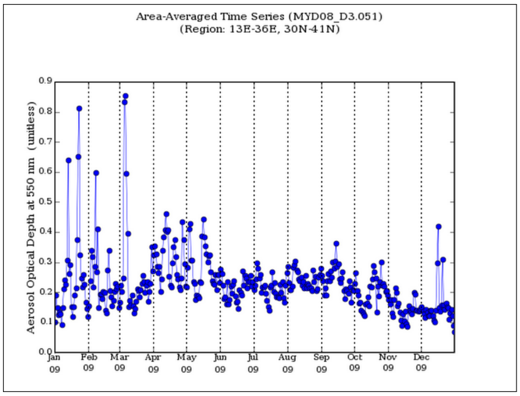


Fig 4. Aerosol Optical Depth for the Eastern Mediterranean during 2009.

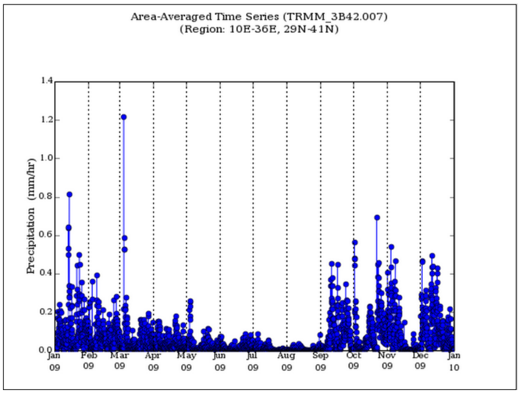


Fig 5. Daily precipitation observed at Eastern Mediterranean during 2009.

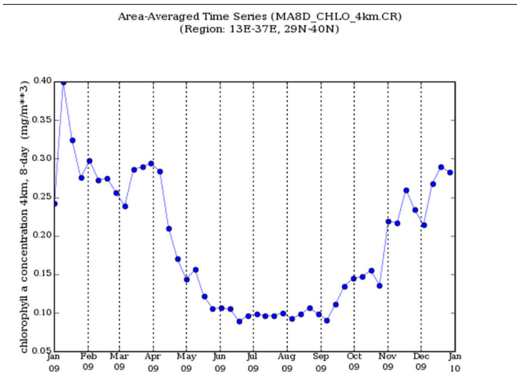


Fig 6. Variation at chlorophyll level at Eastern Mediterranean during 2009.

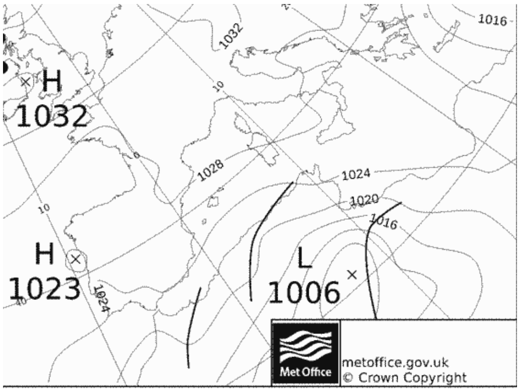


Figure 7. Surface pressure map over the western Mediterranean during 13 March 2014

This specific case satisfies all the necessary preconditioning stages as to enhance the surface waters with the above mentioned reaction products as well as with various amino acids. The receiving body responds to this natural iron fertilizing action via chlorophyll bloom, just like artificial fertilizations, and this can be observed via satellites provided that during the course of maximum bloom the sky is cloud free over the region of interest.

The time phase that is necessary for chlorophyll to reach its maximum levels is about two weeks. But during this time period active surface currents redistributes the chlorophylls along with acting eddies and filaments, as shown in Figure 12 and 13 for 31st March and 1st April 2014, so that the bloom appear to resemble oceanic properties but in fact seeding is performed via two week old wet dust deposition.

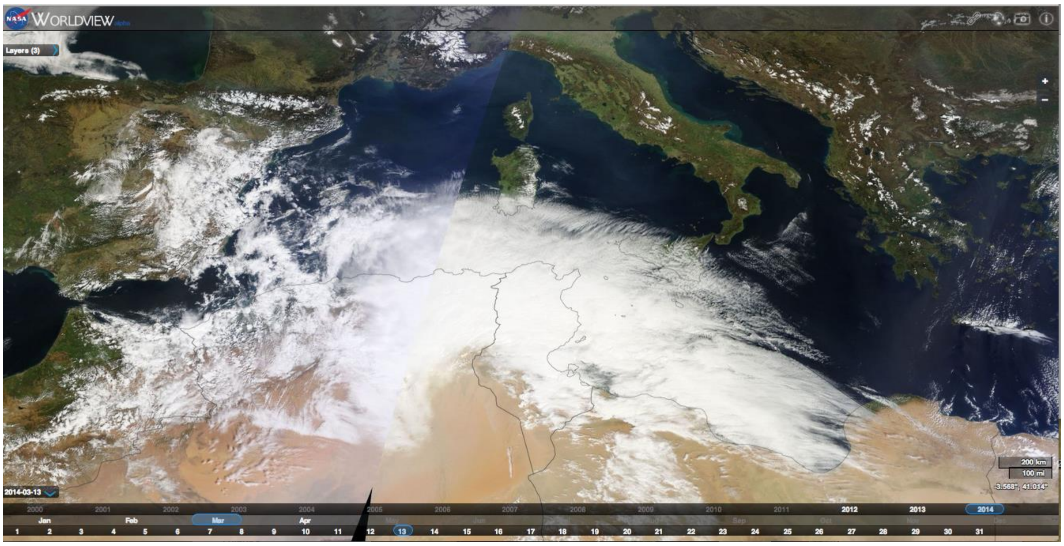


Figure 8. The satellite perspective of the cyclonic depression over Northern Africa during 13th March 2014.

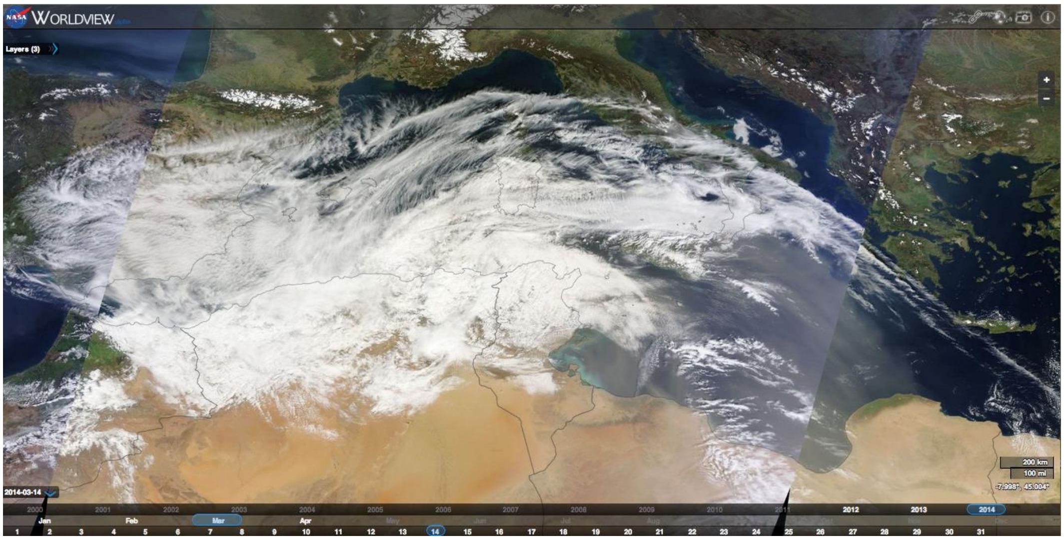


Figure 9. The satellite perspective of the cyclonic depression over Northern Africa during 14th March 2014.

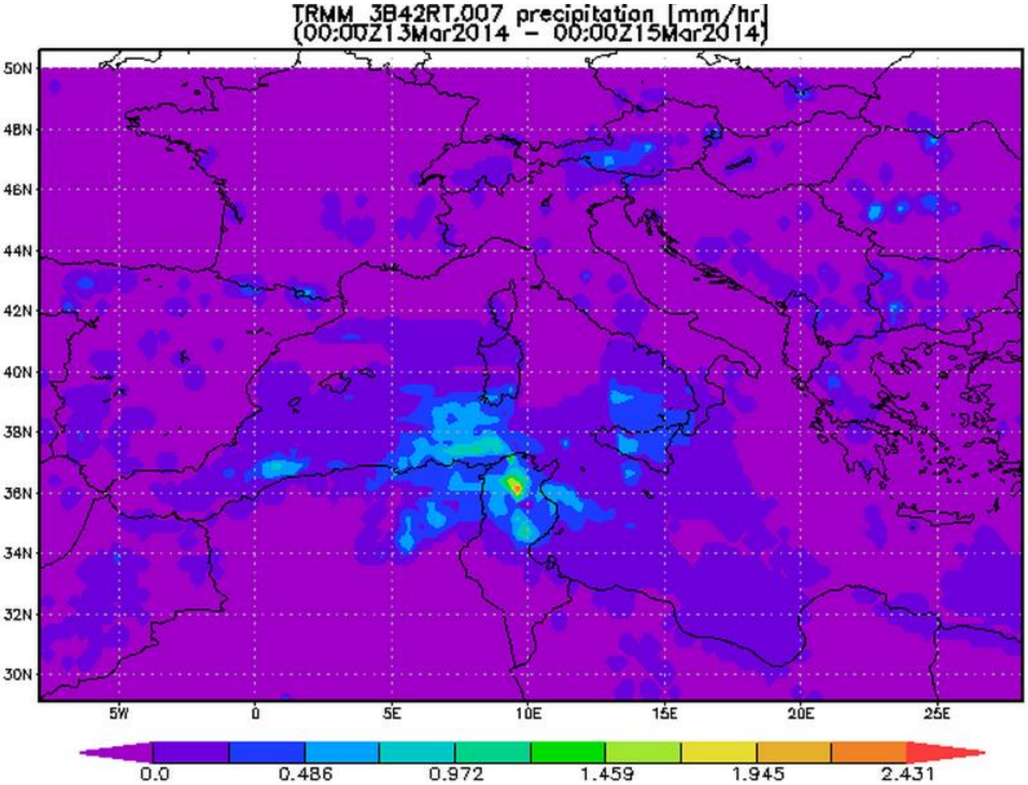
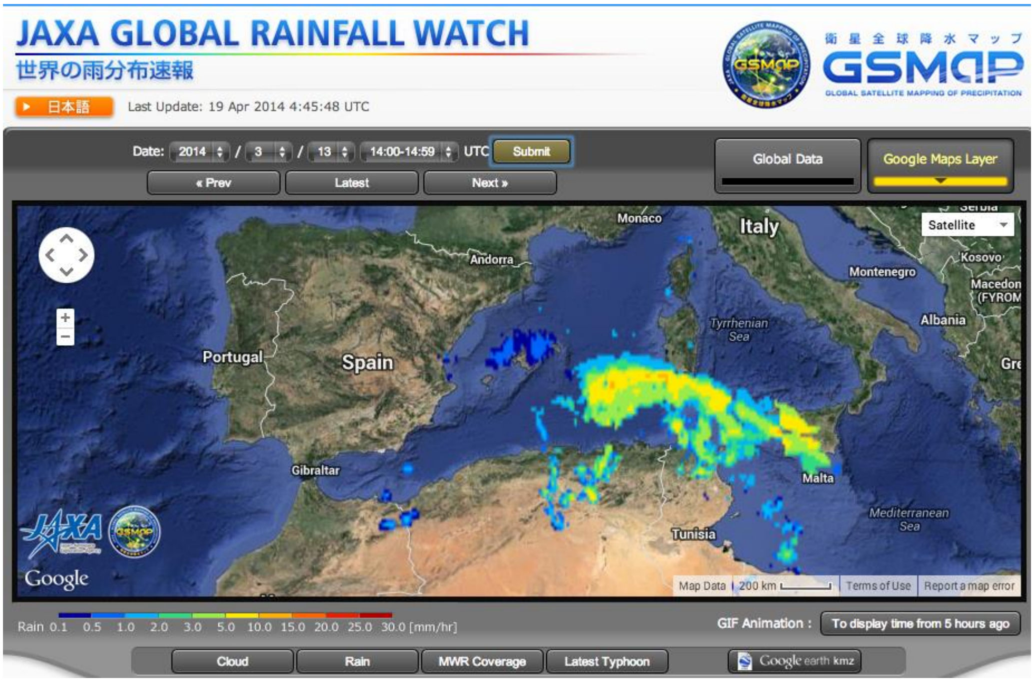


Figure 10. The observed rain events over the Western Mediterranean basin during 13 and 14 March 2014.


Last Update: 19 Apr 2014 4:45:48 UTC

Date: 2014 / 3 / 13 14:00-14:59 UTC

Figure 11. The geographical spread of rain observed at Western Mediterranean on 13 March 2014 from 1400-15:00 GMT.

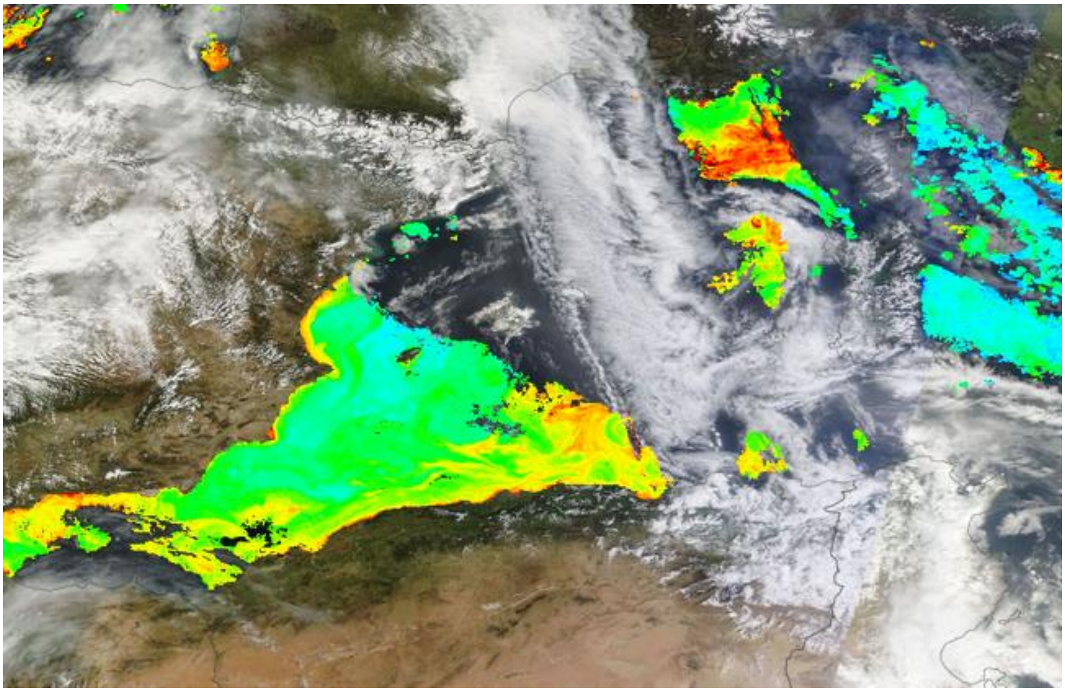


Fig 12. Chlorophyll bloom observed off the coast of Algeria on 31st March

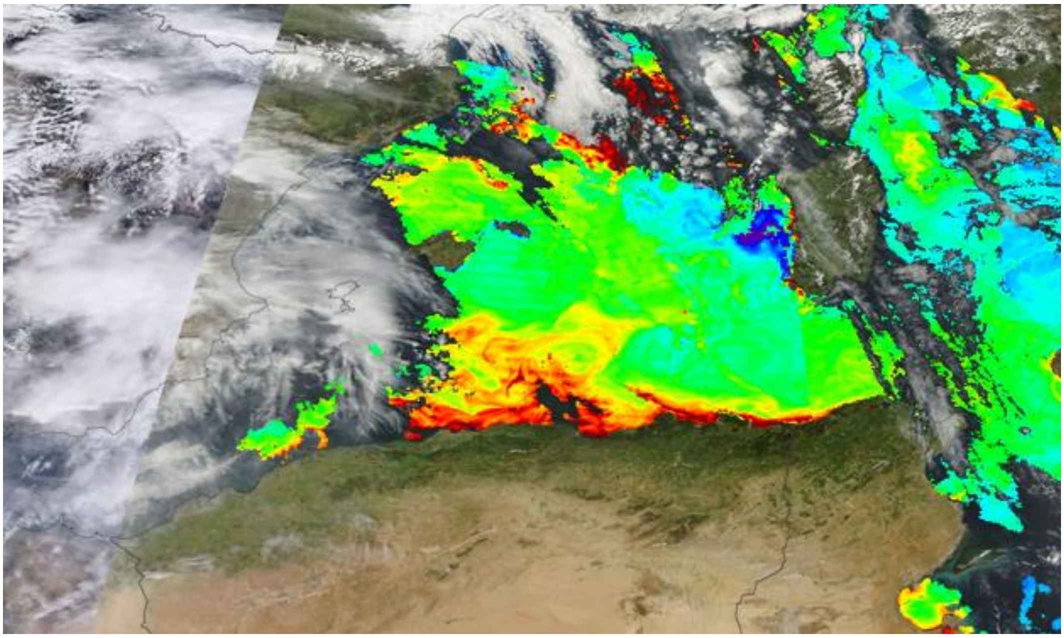


Fig 13. Chlorophyll bloom observed off the coast of Algeria on 1st April 2014.

Conclusion

It can be seen that desert origin dust can trigger natural iron fertilization through the production of dissolved iron within the clouds. The rate determining step is the production of strong reducing agent, oxalate, as an osmosolute by the prokaryotes that exists in ample amounts embedded within the clay minerals and this property is specific to deserts. This new iconoclastic approach will change our understanding of iron enrichment and subsequent algae bloom over the surface ocean except for the regions where algae bloom is supported by upwelling.

Thus, the implementation of this biological aspect into the clouds and its already complex interactions with aerosols may seem yet another challenge for modelers but without this essential aspect the global scale climate models may not be adequate to simulate the real atmospheric processes. This new iconoclastic approach will also alter our understanding of natural carbon dioxide generation mechanisms. This new aspect offers a great potential for the entire scientific community 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.

This new aspect carries even more importance for those developing nations that happen to own such resources, which were so far dismissed as useless land, 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 Fe(II) production within the clouds and enhancing the wet precipitation with Fe(II) and simulating the phytoplankton growth over the oceans, possibly with a stabilizing effect on climate, as suggested by Charlson et al. (1987).

After all, we all have used to irrigate the soil. But seeding the cloud with desert soil or as we put it ‘cloud dusting’ is a new terminology that may likely to open a new era before us, something exactly similar to land irrigation with one major difference, solar irradiation and thousands of meters of optical depth within the clouds as to enhance the bioavailable iron and other essential micronutirnt elements to sustain the microbial metropolises in sky.

Acknowledgement

We acknowledge the use of Rapid Response imagery from the Land Atmosphere Near-real time Capability for EOS (LANCE) system operated by the NASA/GSFC/Earth Science Data and Information System (ESDIS) with funding provided by NASA/HQ.

References

Baker, A. R., & Croot, P. L. (2010). Atmospheric and marine controls on aerosol iron solubility in seawater. *Marine Chemistry*, *120*(1), 4-13.

Charlson, R. J., Lovelock, J. E., Andreae, M. O. and Warren, S. 1987. Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate, Nature, 326, 655-661.

Chen, J., Blume, H. P., & Beyer, L. (2000). Weathering of rocks induced by lichen colonization—a review. *Catena*, *39*(2), 121-146

Guieu. C., Loy¨e-Pilot M. D. Ridame C. and Thomas C. Chemical characterization of the Saharan dust end-member: Some biogeochemical implications for the western Mediterranean Sea JGR,107, NO. D15, 10.1029/2001JD000582, 2002

Griffin, D.W., Garrison.V. H., Herman. J. R., Shinn. E.A. African desert dust in the Caribbean atmosphere: Microbiology and public health. Aerobiologia. 17: 203–213, 2001

Griffin, D. W., Kubilay, N., Koçak, M., Gray, M. A., Borden, T. C., & Shinn, E. A. (2007). Airborne desert dust and aeromicrobiology over the Turkish Mediterranean Coastline. *Atmospheric Environment*, *41*(19), 4050-4062.

Guerzoni, Stefano, Roy Chester, François Dulac, Barak Herut, Marie-Dominique Loÿe-Pilot, Chris Measures, Christophe Migon et al. "The role of atmospheric deposition in the biogeochemistry of the Mediterranean Sea. "*Progress in Oceanography* 44, no. 1 (1999): 147-190.

Hadjialighandi Amir (2011) The investigation of the variations in atmospheric CO_2 levels during the course of Saharan dust transport (In Turkish) M.Sc Thesis. Hacettepe University. Environmental Engineering.179p.

Jickells, T. D., An, Z. S., Andersen, K. K., Baker, A. R., Bergametti, G., Brooks, N. & Torres, R. (2005). Global iron connections between desert dust, ocean biogeochemistry, and climate. *Science*, *308*(5718), 67-71.

Leininger, S., Urich, T., Schloter, M., Schwark, L., Qi, J., Nicol, G. W. & Schleper, C. (2006). Archaea predominate among ammonia-oxidizing prokaryotes in soils. *Nature*, *442*(7104), 806-809.

Levin, Z., Ganor, E., & Gladstein, V. (1996). The effects of desert particles coated with sulfate on rain formation in the eastern Mediterranean. *Journal of Applied Meteorology*, *35*(9), 1511-1523.

Martin, J. H. (1992). Iron as a limiting factor in oceanic productivity. In *Primary productivity and biogeochemical cycles in the sea* (pp. 123-137). Springer US.

Kellogg, C. A., & Griffin, D. W. (2006). Aerobiology and the global transport of desert dust. *Trends in ecology & evolution*, *21*(11), 638-644.

Myriokefalitakis, S., Tsigaridis, K., Mihalopoulos, N., Sciare, J., Nenes, A., Kawamura, K., Segers, A., and Kanakidou, M.: In-cloud oxalate formation in the global troposphere: a 3-D modeling study, Atmos. Chem. Phys., 11, 5761-5782, doi:10.5194/acp-11-5761-2011, 2011.

Rogora, M., R. Mosello, and A. Marchetto. "Long-term trends in the chemistry of atmospheric deposition in Northwestern Italy: the role of increasing Saharan dust deposition." *Tellus B* 56, no. 5 (2004): 426-434.

Ruijter, G. J., van de Vondervoort, P. J., & Visser, J. (1999). Oxalic acid production by Aspergillus niger: an oxalate-non-producing mutant produces citric acid at pH 5 and in the presence of manganese. *Microbiology*, *145*(9), 2569-2576.

Saydam. A. C. and Senyuva. H. Z. Deserts: Can they be the potential suppliers of bioavailable iron? Geophysical Research Letters**.** 29,(11), DOI:10.1029/2001GL013562, 2002

Sorooshian, Armin, Varuntida Varutbangkul, Fred J. Brechtel, Barbara Ervens, Graham Feingold, Roya Bahreini, Shane M. Murphy et al. "Oxalic acid in clear and cloudy atmospheres: Analysis of data from International Consortium for Atmospheric Research on Transport and Transformation 2004." *Journal of Geophysical Research: Atmospheres (1984–2012)* 111, no. D23 (2006).

Sulzberger, Barbara, and Hansulrich Laubscher. "Reactivity of various types of iron (III) (hydr) oxides towards light-induced dissolution." *Marine Chemistry* 50 (1) (1995): 103-115.

Toon. O. B. African dust in Florida clouds. Nature, 427, 623-624, 2003.

Yu, Jian Zhen, Xiao-Feng Huang, Jinhui Xu, and Min Hu. "When aerosol sulfate goes up, so does oxalate: Implication for the formation mechanisms of oxalate." *Environmental science & technology* 39 (1), (2005): 128-133.

Zuo, Yuegang, and Juerg Hoigne. "Formation of hydrogen peroxide and depletion of oxalic acid in atmospheric water by photolysis of iron (III)-oxalato complexes." *Environmental Science & Technology* 26, no. 5 (1992): 1014-1022.