

SOIL AND DUST MINERALOGY: IRON CARRIED BY DUST AND IMPACTS

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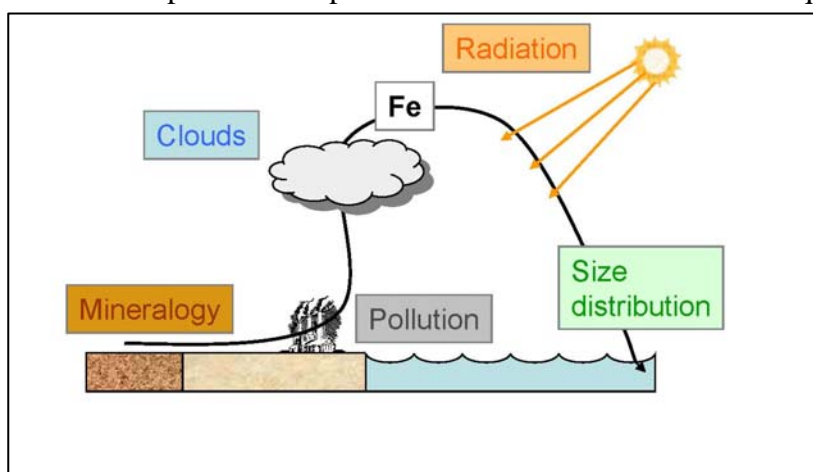
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1. INTRODUCTION

Mineral dust transported through the atmosphere carries iron-rich minerals which may play a role as nutrients if deposited over the open ocean. At soil sources, Fe is almost non-soluble, but its solubility can substantially increase during the atmospheric transport. The soluble Fe form is considered as favorable for the marine bioproduction.

The mineral composition of dust emitted from desert sources is an important factor in affecting the Earth's environment and human health. The colour of arid soils and dust emitted influences the solar radiation absorption and represents a climate/weather-modifying factor. The soil/dust colour depends on the iron content in the iron-rich minerals. Furthermore, iron carried by dust and deposited over the open ocean is key micronutrient in the marine food chain. Finally, it is hypothesized that the meningitis outbreaks in Sahel are linked to the dusty weather season and might be dependent on the amount of iron content in the inhaled mineral dust.

The following are processes identified as possible causes for iron solubilization but of unknown relative importance: exposure to solar radiation and consequent Fe photo-chemical reduction; Fe



solubility increase due to cloud influence; biomass and pollution as agents enhancing Fe solubility; role of dust mineralogy on the solubility process; physical particle sorting by deposition. Figure 1 show schematically to Fe solubility process due to different influences. (Gao et al, 2003; Jickells and Spokes, 2001; Desboeufs et al., 2001, Hand et al., 2004)

Figure 1 Schematic picture of the atmospheric Fe process

2. ATMOSPHERIC DUST-IRON MODEL

Most of the current dust models with added Fe component, developed to study the role of Fe to marine biochemistry after dust deposition, are global, with horizontal resolutions larger than 100 km. The Fe mineralogy at soil sources is typically treated in such models in a simplistic way (e.g. as a constant fraction of 3.6 % or similar).

The aim of our paper is to study the atmospheric Fe process in more details using modelling means and to make the process dependent on dust mineralogy. For that goal we added in the DREAM dust model (Nickovic et al., 2001; Nickovic, 2005) a set of additional Fe-related Eulerian concentration equations for the total Fe (T), for the soluble Fe (S) and for the free Fe fraction (an iron fraction in goethite and hematite). Dust particle size distribution is described by eight bins with effective radii ranging from 0.15-7.1 μm (Tegen and Lacis, 1996). Fe reduction to a soluble form is simulated with a first-order reaction kinetic equation. We assume that the rate coefficient consists of

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two parts: one, associated to processes dependent on cloud and solar radiation (K_{CR}), and another influenced by the mineralogy of dust sources (K_M): $K = K_{CR} + K_M = \frac{1}{\tau_{CR}}(\alpha_C + \alpha_R) + K_M$; parameters α_C and α_R are made dependent on clouds and solar radiation, respectively, τ_{CR} is the characteristic decay time due to cloud and radiation effects, which will be specified later.

Journet et al. (2008) showed that mineralogy is a critical factor for iron solubilization. They demonstrated that the majority of bioavailable Fe in dust originates from clays containing over 90% of the soluble iron, rather than from the iron oxides (e.g. hematite) in spite of having high iron content (50–80%). In laboratory experiments, Shi et al (2011) analyzed soil samples from African dust sources and showed relationship between the degree of chemical weathering (reflected in amount of the free-to-total iron ratio f) and potential Fe solubility $s_{pot} = -22.1 \times f + 15.8$ ($R^2 = 0.44$).

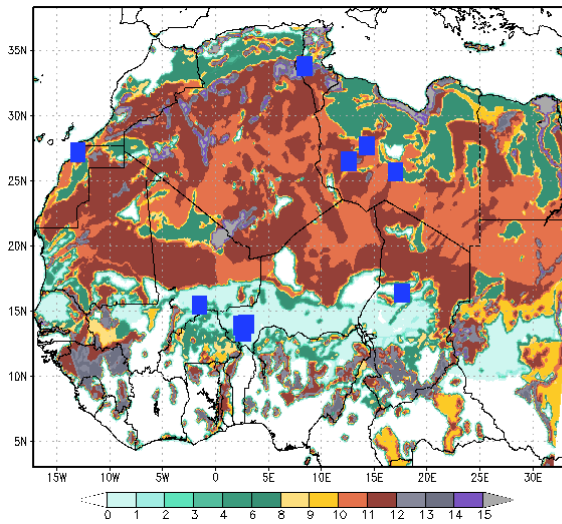


Figure 2 Free-to-total iron ratio f

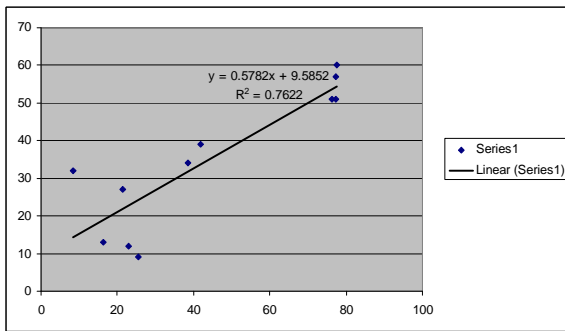


Figure 2 Observed f at soil sample sites and GMINER30 values in these locations

We further assumed that $\tau_{CR} = \tau_M$. With a dust lifetime considered to be of an order of weeks, we specified in the model $t_f = 30$ days as a typical time of Fe exposure in the atmosphere, and obtained τ to be in the range from 20 to 28 days.

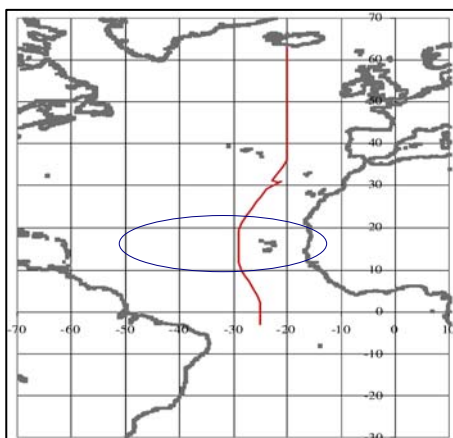
3. MODEL RESULTS

In our study, we calculated the Fe percentages in iron-carrying minerals in illite, kaolinite, smectite, iron oxides (goethite/hematite) and feldspars from the GMINER30 global 1km database (Nickovic et al., 2012)². Figure 2 shows f values mapped from GMINER30; locations of observation sites are also marked. Figure 2 shows the scatter diagram of f observed at 11 sites and values interpolated from GMINER30 in these locations, with good correlation achieved ($R^2 = 0.76$). This is indirect confirmation that GMINER30 data compares well against observations. By integrating the reaction kinetics equation, we obtained $\ln(100 - s_{pot}) = \ln(100 - s_0) - K_M t_f$.

With the solubility in soil sources assumed to be $s_0 = 0.1\%$ we considered $s_0 \ll 100\%$ and evaluated $\tau_M = \frac{1}{K_M} = -t_f \frac{1}{\ln\left(1 - \frac{s_{pot}}{100}\right)}$. This way, we made the Fe solubility process dependent on dust mineralogy.

² Available at <http://www.seevccc.rs/GMINER30/>

To evaluate the model performance, we used data from the July 2003 Atlantic cruise (Buck et al., 2010) when daily samples were dominated only by Saharan dust. Model experiments were conducted to simulate the iron atmospheric cycle along the path of the cruise indicated by the red line in Figures 3 and 4.



Meteorological initial and boundary conditions for the atmospheric model driver were updated every day from the gridded 0.5 deg ECMWF objective analyses archive. Simulated 24-hour dust and iron concentrations from a previous day were used as initial conditions for a current day. The experiment had a zero-concentration “cold start” four days before the starting date of the simulated period characterized by dust conditions in order to remove model spin-up effects. Figure 4 shows geographic distribution of the Fe-related simulated fields valid for 12:00 UTC 26 July 2003. The blue marker in figures indicates the position of the cruise vessel.

Figure 3 Simulation of the Fe cycle for the Buck et al.,(2010) cruise

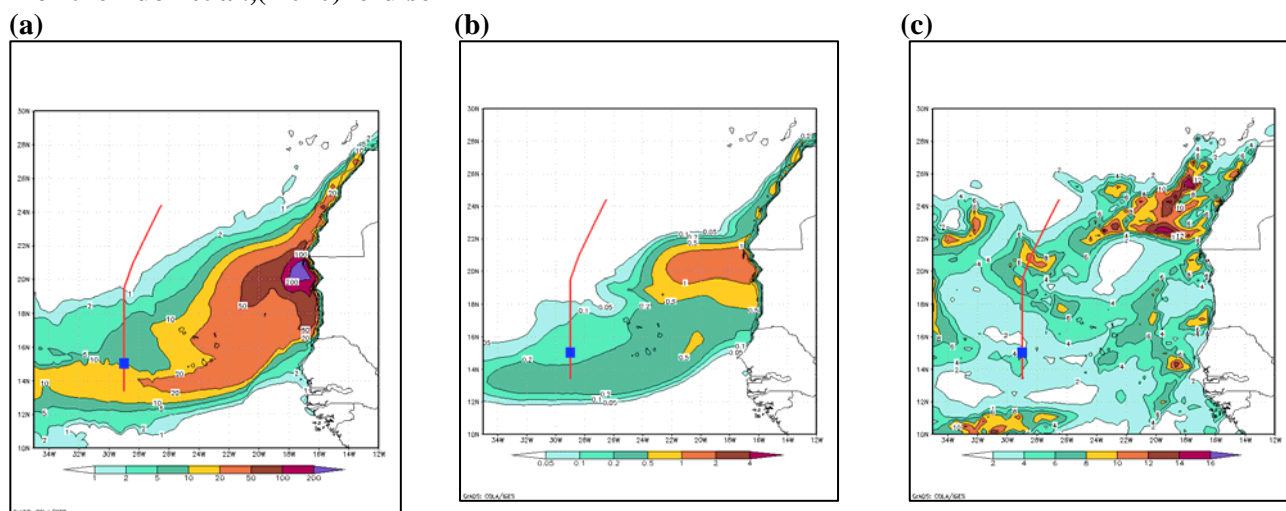


Figure 4 Model simulation valid for 26 July 2003; (a) total Fe ($\mu\text{g}/\text{m}^3$); (b) soluble Fe ($\mu\text{g}/\text{m}^3$); (c) Fe solubility (%)

Fields show high spatial variability, originating from relatively fine horizontal resolution and from detailed mapping of the soil mineralogy used in the model. A striking feature is the existence of very small, local structures in the field of solubility. Figure 5 compares daily values of total Fe and its solubility over the period 21-26 July which Buck et al. (2010) reported as dominated by dust transported from Africa. Simulated total Fe compares against observations within the range of an order of magnitude (Figure 5a). Having in mind that transport patterns in dust models from the emission source region are usually very similar, but the predicted surface level concentration sometimes shows a difference of more than one order of magnitude in model intercomparison experiments (Uno, et al. 2006; Todd et al, 2008), we may consider our result as satisfactory. Concerning the model Fe solubility validation against observation, the simulated values are one may expect for natural non-polluted dust.

4. CONCLUSIONS

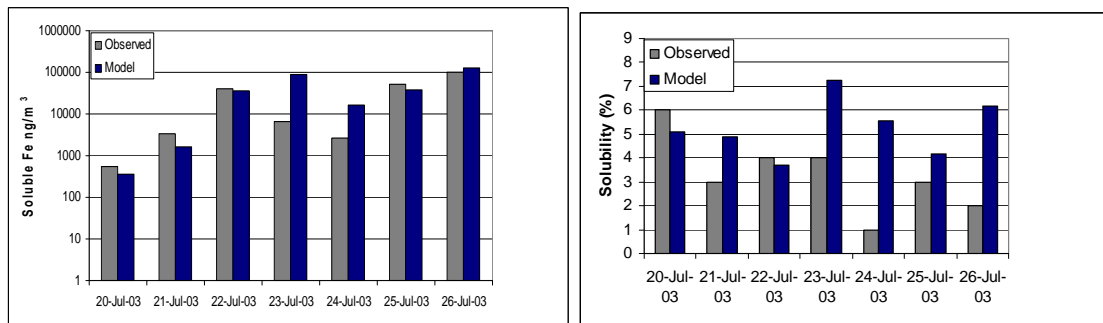


Figure 5 Total Fe and Fe solubility: model vs. observations comparisons along the cruise route

Our study demonstrates the usefulness of using high-resolution modelling approach at regional scale to describe the atmospheric Fe process. It also proposes a parameterization method that makes the Fe conversion from non-soluble to soluble form dependent on dust mineralogy. Further research will include more cruise data for model validation and simulations over longer time scales.

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