In cloud production mechanisms of CO_2 and CH_4

The present level of atmospheric CO_2 concentrations and the results of ice cores undisputedly illustrate the unprecedented historic levels of greenhouse gases. In general, anthropogenic sources and in particular the global power sector, which generates around 40% of all global electricity from coal, is blamed for this rise and actions needs to be taken on an international basis as to combat with this fact. But are we certain about the sources of greenhouse gases?

Here we show that during the course of long range transport of desert dust under the influence of that particular synoptic scale meteorological event the dust particles has a chance to interact with cloud water. Our iconoclastic hypothesis starts with the activation of sub micron sized prokayrotes (10^7 to 10^{35} in number per gram of dust) that are embedded within the clay particles.

Upon contact with cloud water prokaryotes becomes active in minutes and releases oxalate as an osmosolute to their immediate surroundings as shown by (Saydam and Senyuva,2002). Up to date oxalate, one of the most abundant dicarboxylic acids in atmosphere, is still believed to be originated from biogenic hydrocarbons and from anthropogenic sources. But its further known that in-cloud global oxalate net chemical production is calculated to be about 21–37 Tg yr−1 with almost 79 % originating from biogenic hydrocarbons, mainly isoprene. (Myriokefalitakis et al. 2011) Saydam and Senyuva (2002) has shown that oxalate is in fact produced by the prokaryotes embedded within the clay mineral, since upon sterilization by Co^{60} gamma rays oxalate production has ceased, illustrating the impact of biological activity in the production mechanism of oxalate.

As shown by Sulzberger and Laubsherrer(1995), light induced dissolution of Fe(III) (hydr)oxide takes place by using oxalate as an reducing agent. The reaction of iron mineral by oxalate results with the formation of one mole of iron oxide and one mole of water.

$\equiv FeOOH + C_2O_4 \longrightarrow FeC_2O_4 + H_2O$

($\equiv FeOOH$) represents the iron bearing clay mineral,

It should be remembered that these reactions take place following the contact of desert dust particles with cloud water that often occurs far away from source regions. If the solar radiation is above ≥200 Watt/m^2 , that varies latitudinally, then iron oxalate undergoes decarboxylation reaction via absorption of solar light followed by the formation of photoproducts through dissociation and decarboxylation;

$FeC_2O_4 \longrightarrow Fe(II) + CO_2 + CO_2\bullet$

each of these end products have very essential roles in atmospheric chemistry.

Carbonyl is a reductant and reacts either with 0_2, or with another surface or dissolved Fe(II) species or with another $CO_2\bullet$ and forms another C_2O_4 acting as an feedback mechanism that can react with clay mineral as to form yet another iron oxalate.

Reduced iron Fe(II) is the bioavailable form of iron. It should be noted that during the course of the ocean seeding experiments $FeSO_4$ is used seed the oceans artificially as to prove the Martin's iron hypothesis. Thus as a result of desert dust cloud interactions the atmospheric water is enhanced with respect to reduced iron. Upon wet precipitation the receiving body responds to such events by enhancing chlorophyll concentrations (Saydam, 2014).

Based on these reaction schemes, we have shown that during the desert dust transport events atmospheric CO_2 increases during the day time in line with our hypothesis and we have used 17-18 February 2010 dust transport event as a case study. As shown in Figure 1, the entre basin is dominated by Saharan dust and the dust pulse and clouds persisted over the region on 18 February as well.

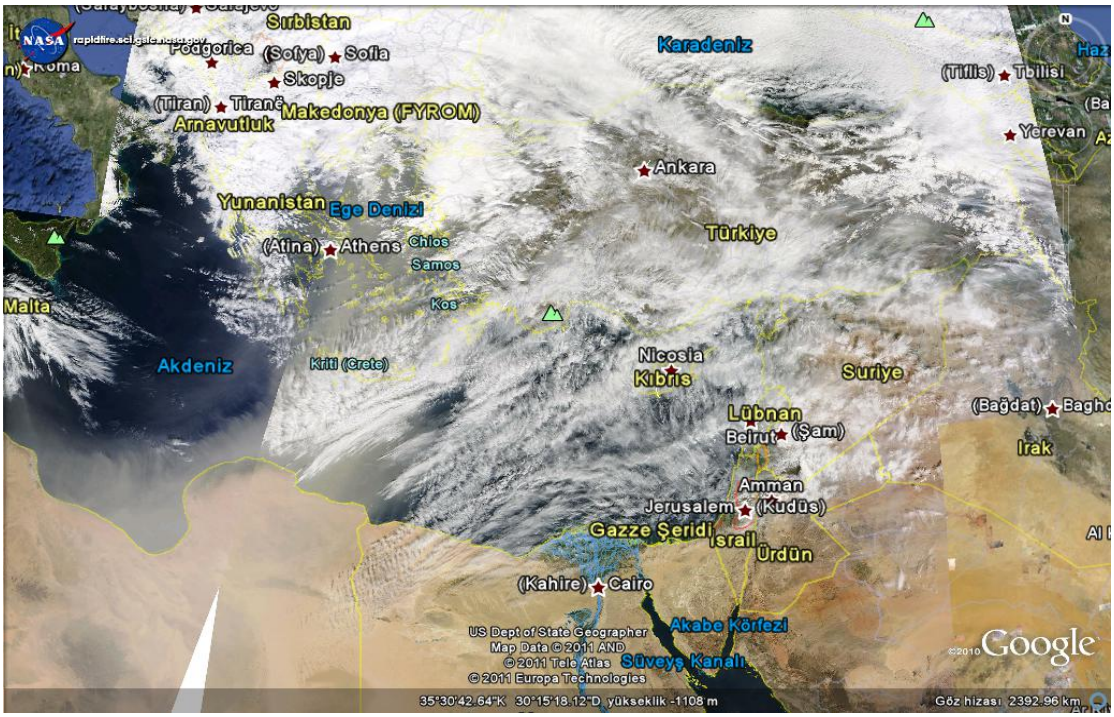

Figure 1. 17 Feb., 2010, dust transport event as recorded by MODIS satellites. It can clearly be seen that the entire Eastern Mediterranean and Anatolia is covered by desert dust and clouds.

The results of continuous measurements of CO_2 during 17-18 Feb 2010 is shown in Figure 2.

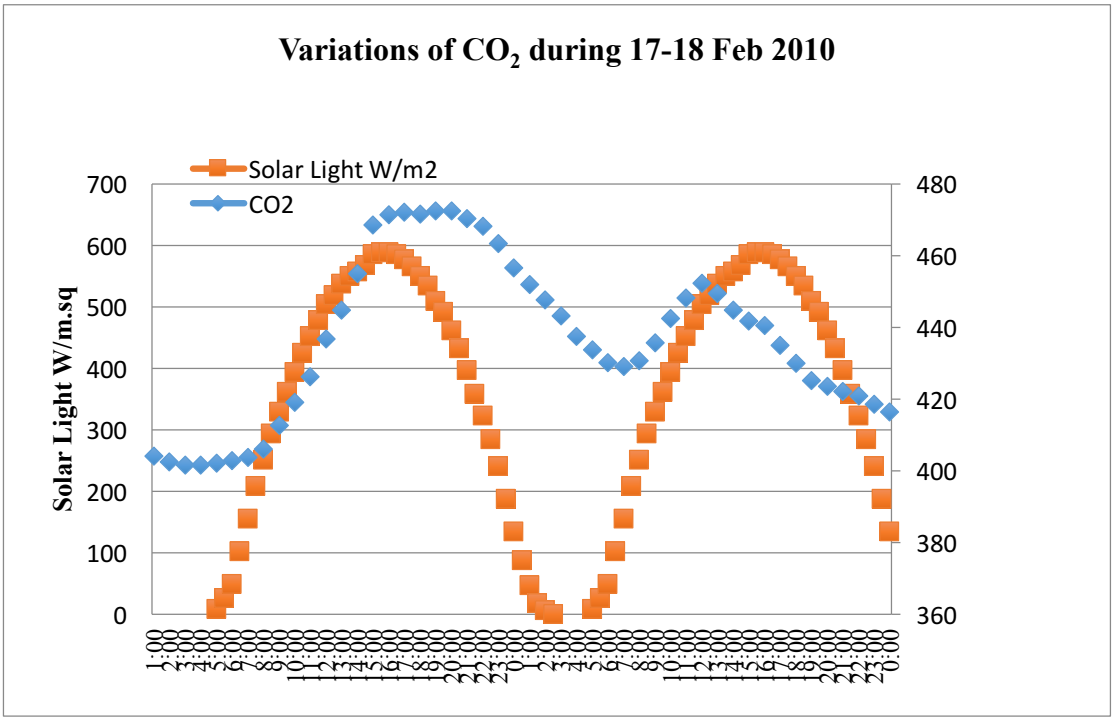

Figure 2. Solar light intensity and CO_2 change as measured at 1050 m at Hacettepe University Beytepe, Ankara-Turkey monitoring station the during 17 and 18 Feb. 2010 dust transport event.

It can be clearly seen that the variations in CO_2 concentrations is in parallel with the solar light intensity and peak values is reached in late afternoon due to enhanced levels of decarboxylation reaction.

Had our station adopted the procedures of conventional WMO monitoring stations, then nearly all CO_2 measurements made during the course of 17 & 18 Feb 2010 would have been discarded in favor of the artificial limits set by WMO/WDCGG, and one can safely assume that similar inaccuracies will pertain to all WMO records collected to date. The empirical limit set by WDCGG for hourly ΔCO_2 is 0.3 ppmv and with this limitation all the data would have been excluded from the data archive despite the real contribution that this neoformed CO_2 actually makes to the global CO_2 budget.

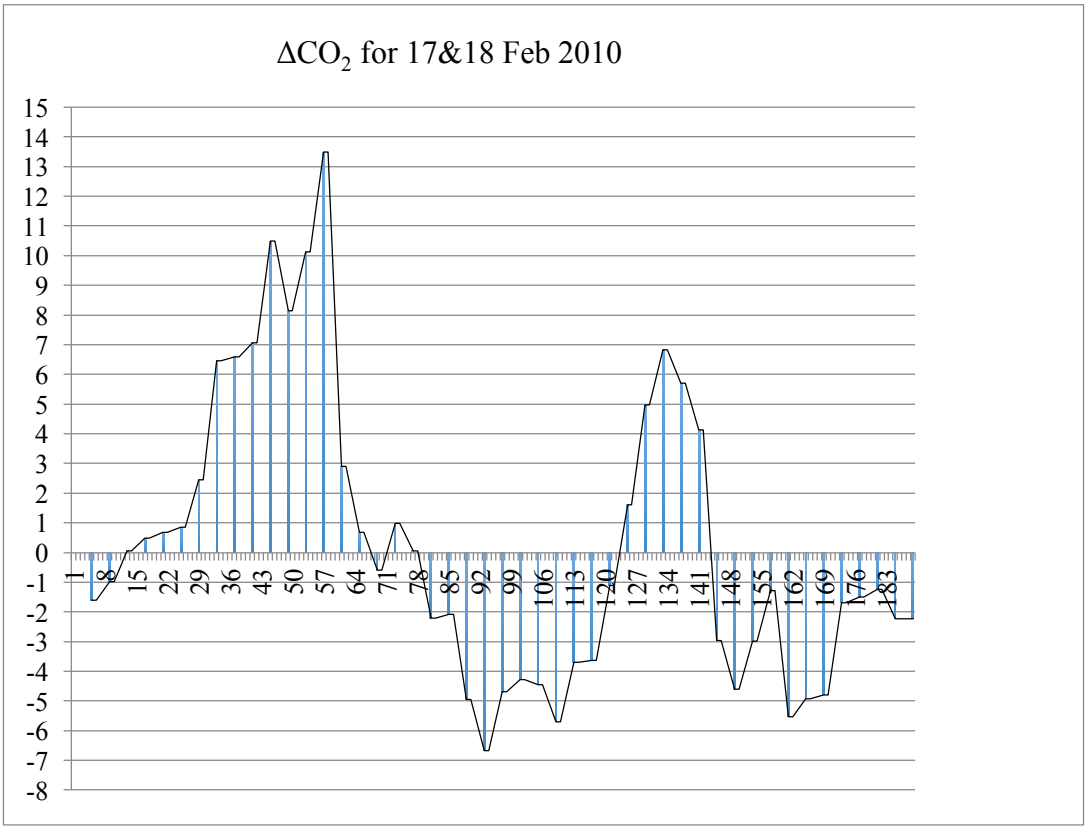

Figure 3. The hourly rate of CO_2 change observed during the course of 17-18 February 2010 Saharan desert dust transport across Turkey.

It should be noted that the empirical limit set by WDCGG for hourly ΔCO_2 is 0.3 ppmv and with this limitation all the data would have been excluded from the data archive despite the real contribution that this neoformed CO_2 actually makes to the global CO_2 budget.

A major dust storm in northern China in April 1998 was observed on satellite imagery crossing the Pacific over a period of five days (Husar., et al. 2001; Tratt,et al 2001) The satellite imageries have shown that the dust pulse has reached over the Minamitorishima Island on 22-23 April 1998. The results of the continuous CO_2 and CH_4 measurements were given in Figure 4. The dust pulse over the mainland was the only major event took place and there was no report of any major accident that can release CO_2 or CH_4 into the atmosphere.

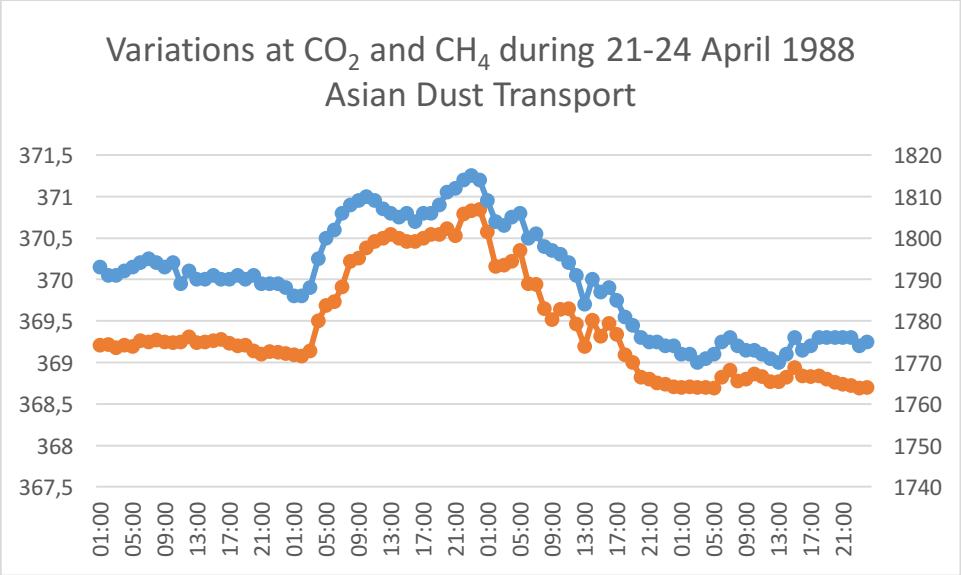

Figure 4. Variations of CO_2 and CH_4 as measured at Minamitorishma Island during 21-24 April 1998.

It can be seen that upon arrival of dust pulse over the island both CO_2 and CH_4 levels increased in parallel. Our iconoclastic approach can explain the variations observed at CO_2 via in cloud decarboxylation reaction mechanisms but the formation of CH_4 as shown in Figure 4, also claims the similar in cloud production processes. Scientific community so far has not tackled with this issue at all since formation of methane under anaerobic conditions has not been dealt with except few studies (Keppler et al., 2006;2009; Althoff et al.,(2010).

Mace et al.,(2003) have further shown that rain samples originated from Sahara contains various amino acids and the individual amino acids contributing ~75% of the total amino N suggest the presence of primitive organisms in the aerosol samples analyzed. Since bacteria and fungi are thought to be associated with African dust (Griffin et al.,2001;2007) and since an atmosphere dominated by desert sources persisted during the sampling campaign, it is likely that individual amino acid totals within aerosol samples were influenced by these organisms. Though the logical explanation can be accepted as above the formation of amine group is still remains to be one of the puzzles of the mother nature.

Thus one has to find means that can control not only the in cloud formation of carbon dioxide in parts per million levels but also methane and amine groups in parts per billion levels as well. Methane further complicates the matter since methane is believed to be formed under anaerobic conditions. To address this problem once again we have turned our attention to dust i.e., to soil and we have noticed the following vital structure that forms the outer shells of fungi's, chitin.

The prokaryotes embedded within the clay mineral also contains fungi's and the outer shell of fungi's is made of chitin. Chitin is a is a long-chain polymer of a N-acetylglucosamine, a derivative of glucose: The molecular formula is shown below in Figure 5.

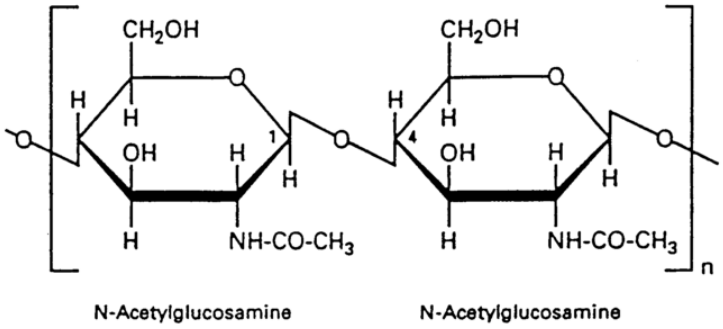

Figure 5. Molecular structure of chitin.

Thus if we can manage to disintegrate chitin then we may have valuable amine groups and methyl radical which is eventually result with the formation of methane. We have hypothesized that the oxalate produced by the fungi's can also be use to disintegrate the chitin. Thus we have set up an experiments by using Saharan desert soil samples encapsulated in headspace cups sealed with nitrogen air. The initial samples as analyzed by GC/FID, did not result with any sign of methane but within 24 hours we have managed to show that methane is produced in few ppm levels within headspace cups under aerobic conditions as shown in Figure 6.

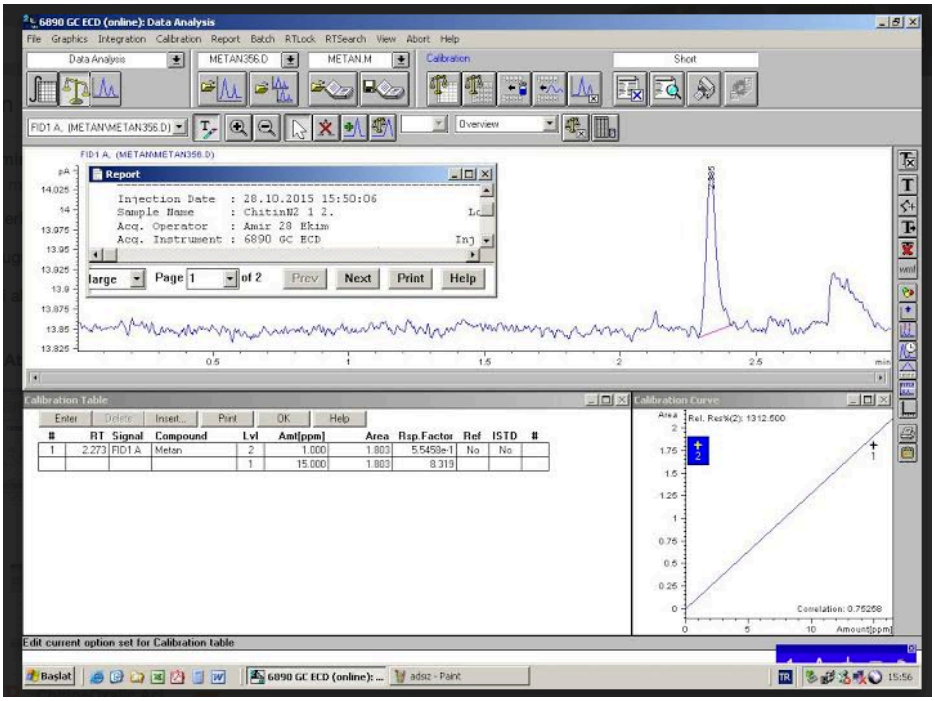

Figure 6. The chromatogram of methane as observed by GC/FID system equipped with CarbonPLOT capillary column.

This property is being measured by all atmospheric stations enlisted at WMO/WDCGG as well as via FP6/Carboeurope and present ICOS projects, but the data is either artificially ignored due to empirically set limit by WMO both for CO_2 and CH_4 or the parallel variations is totally ignored since there is no way to explain this simultaneous variations of these greenhouse gases with our existing knowledge.

We show here for the first time that desert dust and cloud interactions result in the formation of significant amounts of neoformed (i.e., “natural”) carbon dioxide and methane under oxic conditions within typical synoptic scale cyclonic depressions. We highlight the importance of dust cloud interactions as a source of significant amounts of “natural” carbon dioxide and methane.

This discovery offers the opportunity for a reassessment to be made of the global greenhouse gas budget. Though the global rise in CO_2 levels (Keeling curve) over the last two centuries is established, those measurements encompass a so far unrecognized or artificially eliminated natural source of CO_2 that is highly relevant to the assessment of the magnitude of human emissions.

The reason why the scientific community has not hitherto taken cyclone-neoformed CO_2 and CH_4 into account is derived relates to the universal use of an empirically determined value set by WMO/WDCGG for the selection of valid hourly CO_2 and CH_4 data. The relevant WMO rule states that, "the differences from both adjacent hourly data don't exceed the value 0.25 ppm for CO_2 and 0.6 ppb for CH_4". By uncritically adopting this restraint, previous dust cloud studies have suppressed the actual CO_2 and CH_4 variations that do in fact occur.

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