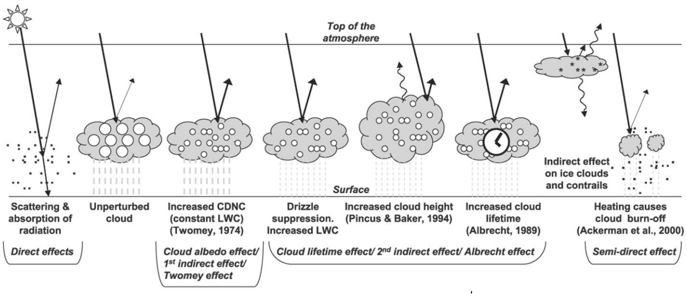

Articles

ARTICLES › HOW CLEAN IS THE NATURAL ATMOSPHERE?

How clean is the natural atmosphere?

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Today, many people know that carbon dioxide emissions are the cause of climate change. What most people don’t know, however, is how different our planet is now when compared to the planet of the unchanged pre-industrial times.

The reason for such difficulty resides on the difference between the simple perception of change and quantification of change within defined a reference time, which is far from simple. In fact, to correctly estimate the change the atmosphere has been subject due to anthropogenic emissions depends on the definition of a �ÛÏclean atmosphere�Û� reference state, or a given moment of our history when the atmospheric composition was dominated by natural sources instead of anthropogenic ones. Once that reference state is determined, it is possible to estimate the difference between natural and perturbed conditions. Usually, this reference has been assumed to be the atmospheric composition prior to 1800, when the industrial era had not yet started and anthropogenic emissions were not sufficient to induce significant changes in the atmospheric functioning.

At the present, there is a scientific consensus that the Earth is warmer than it was in 1850. The Fourth Assessment Report of the Intergovernmental Panel on Climate Change (AR4-IPCC, 2007) points out this temperature increase is the net effect of human-induced changes in the planet, and that it resulted in a radiative forcing of +1.6 [+0.6 to +2.4] W.m-^{2}. The most obvious consequence is the rise in global mean temperature. However, one has to keep in mind that climate is much more than temperature. Further, it is not straightforward to assign correctly a cause-effect connection between anthropogenic activities and changes in other climatic parameters such as wind speed and direction, humidity and rain volumes, and dry and wet season partitioning throughout the year. Several uncertainties remain when future scenarios are debated, especially the potential changes in the properties of clouds.

Clouds play a key role in the future climate of the world. They reflect about one third of the incident solar radiation, thus cooling the planet. On the other hand, clouds also heat the atmosphere by retaining infrared radiation emitted by the Earth's surface. Beyond that, changes in cloud patterns also could induce modifications in the hydrological cycle both in global and regional scales, with very serious consequences to agriculture, water supply and natural disasters like floods and droughts. Therefore, the issue of how to quantify the change becomes much more complicated due to the poor records of cloud properties over the 150-year period.

There are several ways for clouds to be changed. The main agent acting in cloud formation is the general circulation of the atmosphere. If global wind patterns come to change in a warmer planet, it is certain that the present cloud cover climatology will be significantly altered. However, it is possible that we have already induced changes in cloud properties due to the enhancement in the global emission of aerosol particles.

Image showing a schematic diagram showing the various radiative mechanisms associated with cloud effects that have been identified as significant in relation to aerosols. Image Credit: IPCC

FIGURE 1: SCHEMATIC DIAGRAM SHOWING THE VARIOUS RADIATIVE MECHANISMS ASSOCIATED WITH CLOUD EFFECTS THAT HAVE BEEN IDENTIFIED AS SIGNIFICANT IN RELATION TO AEROSOLS. IMAGE CREDIT: IPCC

The role of aerosols in the properties of clouds is critical. There is no doubt that clouds form under air masses saturated with water vapor, and that this saturation is mainly due to dynamical movements of the atmosphere. Going into the micro-scale, the initial number of droplets in the early development stage of the cloud is defined by the budget of atmospheric particles that are able to nucleate droplets, also known as the CCN or Cloud Condensation Nuclei, which are a fraction of total airborne particles. The more CCN in the atmosphere, the higher the number of droplets and the smaller their size. This difference, which takes place in the initial stages of the formation of the cloud, influences significantly the whole cloud life cycle and its radiative properties. In Figure 1, a schematic diagram shows the most known effects of aerosols on cloud properties. The Twomey effect is related to the enhancement in cloud albedo due to the presence of more droplets at the same amount of liquid water. The Albrecht effect states that clouds with more and smaller droplets have longer lifetimes and drizzle suppression in comparison to unperturbed clouds. The semi-direct effect (Ackerman et al, 2000) refers to changes in the thermodynamic profile of the atmosphere. For a deeper explanation of each effect, see Lohmann and Feichter (2005).

Clouds also change aerosol properties. Once the CCN is ingested in the cloud base and liquid water involves it in a droplet, aqueous-phase chemical reactions occur. Modeling studies have shown that about half of the sulfate particles, which play a critical role in acidic precipitation in urban environments, and in the backward reflection of incident solar radiation to the space, are produced inside the cloud environment. Thus, clouds play an important role in the chemical transformation of aerosol particles. These examples show how complex the interactions are within the context of the Earth system, and how hard it is to estimate changes in clouds in the context of changing climate.

The first step to infer the actual change is to stipulate two reference points, the perturbed condition and the natural situation, in the climate history. Polluted areas represent the perturbed condition due to its typical high aerosol concentration. The determination of the natural condition is more complicated. When dealing with the particular interaction between aerosols and clouds, one has to keep in mind that the lifetime of aerosols in the atmosphere is typically less than one or two weeks due to removal from the atmosphere by gravitational settling, turbulent transport from atmosphere to ground and wet deposition. Aerosols can be transported very far from sources, sometimes thousands of kilometers from the original emission areas. As shown by Andreae (1983, 2007), few places on Earth are free of the influence of aerosol plumes and could be considered as representative of the natural atmosphere, including Polar Regions, oceanic regions far from coastlines, and the Amazon basin during the wet season. Atmospheric properties at these places allow us to establish a baseline chemical reference for the clean atmosphere.

These regional characteristics of the pollution level become clearer when we look at the global distribution of aerosols in Figure 2. The figure shows, for the period January-June of 2010, the average global Aerosol Optical Depth (AOD) retrieved from the orbital Moderate Resolution Imaging Spectroradiometer (MODIS) sensor. The minimum levels of AOD are found in oceanic areas. Into the continents, the Amazon Basin presents AOD values smaller than 0.1, which are similar to the cleanest oceanic areas. This is completely different than the polluted condition observed over Asia, especially India, China and the southeast portion of the continent, and the western coast of Africa, where AOD values higher than 0.9 were detected.

Map showing average global AOD for the year 2010, retrieved from MODIS measurements. Source: NASA via Giovanni portal. Image Credit: Acker and Leptoukh, 2007.

FIGURE 2: AVERAGE GLOBAL AOD FOR THE YEAR 2010, RETRIEVED FROM MODIS MEASUREMENTS. SOURCE: NASA VIA GIOVANNI PORTAL. IMAGE CREDIT: ACKER AND LEPTOUKH, 2007.

Precipitation chemistry in remote areas

Without the influence of anthropogenic emissions, natural sources of gases and aerosols dominate the atmospheric composition. Seasalt aerosols are the most important influence in remote oceanic areas. During the wet season in central Amazonia, when biomass burning is absent, the emission of primary biogenic particles by the vegetation, such as spores, fungi, leaf debris and pollen, provides the majority of aerosol mass. This is complemented with episodic inputs of Saharan dust when adequate meteorological conditions are established, and is a good example of how the transport of particles acts on the global scale.

Atmospheric processes influence rainwater chemistry in two ways. The first way is in the formation of cloud drops, when aerosol particles act as cloud condensation nuclei and contribute to the composition of the initial drop. The aqueous environment of the drop also is adequate for the absorption of soluble trace gases, working as a catalyst to many chemical reactions possible only in the aqueous-phase. Biotransformation by microorganisms also occurs during that stage.

The second mechanism takes place when precipitation begins. Falling raindrops collide with airborne aerosols below cloud base, collecting these particles and adding matter to raindrops. This mechanism of aerosol removal is one of the major processes by which the atmosphere is cleaned. The final result of rainwater chemistry is the combination of these two processes named rainout, or in-cloud, and washout, or below-cloud. In short, precipitation chemistry is the net result of the aerosol life cycle within the hydrological cycle.

As one could expect, precipitation chemistry is completely different in remote, rural agricultural and urban areas. Mean concentrations of the most commonly measured ions in rainwater in very different environmental conditions are shown in Table 1. It is important to note that this list is far from complete. Actually, it is possible to measure a myriad of chemical components in addition to the ions shown here. Nevertheless, the data set shown in Table 1 is enough for the purposes of this article. They refer to the soluble fraction, most of them measured with ionic chromatography or similar techniques.

Once primary and secondary aerosol sources are related to the surrounding environment, each ion can be associated to different processes. Sulfate is one example, where, in urban areas it is associated to acidic precipitation due to vehicular emissions; and in a remote oceanic area, the potential process to incorporate it to rainwater is the production of dimethyl sulfide by phytoplankton and subsequent transformations in the atmosphere ⍰ÛÒ including cloud processing.

The first five columns in Table 1 correspond to remote locations. Even between these sites the chemical profile of rainwater differs significantly. For example, magnesium and calcium concentrations in Poker Flat, Alaska, are one or two orders of magnitude smaller than rainforest or oceanic sites. This is an indication of the strength of biogenic emissions in rainforest area, as well as the presence of these ions in seawater for the case of oceanic sites. Similar but smaller differences can be also observed for potassium and ammonium. For other ions, the concentrations are pretty similar with the exception of sodium and chlorine in oceanic areas, which are the highest for all sites. These differences give us an indication of the chemical profile of each natural source and its emission characteristics.

At a first glance of Table 1, note how remarkable the proximity in pH among all kinds of sites, except Beijing due to reasons to be discussed later. It varied from 4.4 in Piracicaba, to 4.96 in Alaska. Liquid water in the natural atmosphere is acidic with a pH of 5.6 due to the presence of carbon dioxide. Therefore, rainwater has an acidic characteristic both in most remote and polluted sites. But, if natural water is acidic, why worry about acid rain?

There are two answers to this question. First, most acidity in polluted areas is related to strong acids, like sulfuric and nitric acids, that aggressively acidify water bodies and cause the deterioration of buildings. On the other hand, in pristine locations the acidity is mainly associated to weak, organic acids like acetic and formic, which are the end product of several chemical transformations of naturally emitted compounds from the biome. As expected, they have no less of a negative impact on the ecosystem.

Second, the actual impact of acidity in polluted areas is not promptly achieved by pH due to the buffering capacity of ammonia ($H^+ + NH_3$ � Õ NH_4^+) and calcium carbonate ($CaCO_3 + H_2SO_4$ � Õ $CaSO_4 + H_2O + CO_2$). Thus, the presence of ammonium and calcium could mask the actual acidification potential of rainwater.

In spite of the differences between the remote sites, when they are compared to regions under the influence of anthropogenic emissions, the differences are huge. In the agricultural site of Piracicaba the nitrogen compounds like ammonium and nitrate are present in higher concentrations than at any other site. This enrichment is related to the use of fertilizers in soils. The level of sulfate is also higher than at remote sites, and is related to biomass burning at sugar cane culture areas before harvesting. The enhancement in the levels of these anions partially explains the highest concentration of hydrogen and the lowest pH among all displayed sites.

Table showing Volume Weighted Means (VWM) concentration of most commonly measured ions in rainwater in different regions around the world (given in �� eq.l-1). Ac- and Fo- are acetate and formate, respectively. Last line is the annual mean precipitation in mm, and the �ÛÏnss�Û� prefix means the non-sea-salt fraction. Source data: 1Pauliquevis et al. (2012); 2Galloway et al., (1982); 3Lara et al., (2001); 4Rocha et al. (2003); 5Fornaro et al. (2003); 6Yang et al. (2012) and 7Okuda et a. (2005).

TABLE 1: VOLUME WEIGHTED MEANS (VWM) CONCENTRATION OF MOST COMMONLY MEASURED IONS IN RAINWATER IN DIFFERENT REGIONS AROUND THE WORLD (GIVEN IN ÅMEQ.L^{-1}). AC- AND FO- ARE ACETATE AND FORMATE, RESPECTIVELY. LAST LINE IS THE ANNUAL MEAN PRECIPITATION IN MM, AND THE �ÛÏNSS�Û� PREFIX MEANS THE NON-SEA-SALT FRACTION. SOURCE DATA: [1]PAULIQUEVIS ET AL. (2012); [2]GALLOWAY ET AL., (1982); [3]LARA ET AL., (2001); [4]ROCHA ET AL. (2003); [5]FORNARO ET AL. (2003); [6]YANG ET AL. (2012) AND [7]OKUDA ET A. (2005).

The last three columns correspond to urban polluted atmospheres. As in the case of natural areas, they are very different, as pollution sources are not the same in all cities. The high pH of 6.0 in Beijing stands out because it is less acidic than the atmospheric background although nitrate and sulfate are present in high concentrations in the Beijing atmosphere. The nitrogen dioxide and sulfur dioxide emissions that react to form nitrate and sulfate originate from activities such as vehicular emissions and coal burning. However, the buffering potential is also high in Beijing: concentrations of ammonium and calcium in Beijing were ten (five) times higher than observed at Sao Paulo (Tokyo), thus neutralizing the available acidity. Ammonium is mostly related to biomass burning, biological processes, chemical fertilizers, livestock breeding and energy consumption, whereas calcium comes mainly from crustal origin. Although Beijing has presented the highest concentrations of ions, the total amount that reaches the surface and water bodies is the total wet deposition, or the product between concentration and precipitation volume. Rain volume at Beijing was 441 millimeters per year, whereas in Sao Paulo it was 1,300 millimeters per year, and 1,210 millimeters per year in Tokyo. Even considering this approximate factor of 3, the total deposition at the Chinese capital would still be the highest once that for most of ions the observed concentrations were more than three times higher.

Lastly, we will take a look at organic acids, especially acetic and formic acids. Most studies do not measure these acids due to analytical issues. However, depending on the location of the investigated environment, they can play a key role in the acidity profile, as is the case in the precipitation chemistry at Sao Paulo were most of the vehicular light fleet employ �ÛÏgasohol�Û� or pure ethanol as fuel. As shown by Fornaro et al. (2003), different than most big cities around the world where the acid precipitation is more closely related to the strong sulfuric and nitric acids, in Sao Paulo acetic acid and formic acid were responsible for 44 percent of the potential acidity. In Brazil, gasoline is not sold in its pure state but as a mixture of gasoline and ethanol, referred to by some as gasohol. The authors state this significant contribution of organic acids to acidity occurs due to a combination of direct emission of lower carboxylic acids and aldehydes from light vehicles and favorable conditions to photochemical transformations due to the high ozone concentration and intense solar radiation typical of low latitudes. This is one of the net impacts of the extensive use of this fuel matrix, and adds more complexity to the evaluation of environmental impacts of so-called biofuels.

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