The Nanoscience of Clouds, Rain and Rainmaking

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In these days of droughts and fears of climate change it is instructive to look at the physical processes involved and to see what might be done to aid the future of the human race, and more immediately of Australia.

The range of scales is immense. At the high end we are looking at changes in the ice caps near the North and South poles, at the global ocean and atmospheric circulation patterns and, on a shorter time scale, at the motion of weather patterns around the globe. The length scale in each of these cases is in the thousand kilometre range, and this is not the subject of the present article, though we shall venture into the kilometre range.

At the mid-scale of tens of kilometres we observe the formation of clouds, their growth, and sometimes the development of rain, hail or snow, and this will concern us. At even smaller scales we examine cloud droplets with diameters initially in the ten micrometre range, and then their development into millimetre-sized raindrops or snowflakes, while the smallest scale leads to consideration of the nanometre-sized particles that nucleate the formation of cloud droplets and sometimes their conversion to ice crystals.

Let us begin at the most conveniently observed cloud-sized kilometre scale. How do clouds form and what is their inner structure? The quick answer is simple: warm moist air rises, reaches the dew point determined by its initial humidity, and then condenses to a population of small droplets. In the absence of condensation, the "dry adiabatic lapse rate" for cooling of air as it expands upon rising is about 1°C per hundred metres. When condensation begins, latent heat is evolved and the "wet adiabatic lapse rate" is established, this depending on temperature but being considerably less than the dry adiabatic rate. The air in the condensing cloud therefore rises much more rapidly, entraining dry air from its sides as it does so, to produce a typical cumulus cloud that may be as much as 5km in depth. In an alternative scenario, the rising cloud may encounter a temperature inversion, with a blanket of warmer air lying over the colder air below, so that even the wet adiabatic is inadequate and the cloud spreads horizontally to form a stratus cloud layer.

The existence of adequate clouds is, of course, essential for rainfall, whether natural or artificially induced. This is controlled by global climate changes on time scales of hundreds to thousand of years and by global and regional weather variations on time scales of days to years.

The shape and size of clouds provides a great field of study for atmospheric scientists and artists, but here we want to look much more closely and examine the droplets within the cloud. How exactly do they form? How big are they and what is their concentration? Why do some clouds rain and other do not? Is there anything we can do about it? It is here that nanoscience makes its entrance.

Cloud Droplet Nucleation

Let us first consider the process by which a volume of air supersaturated with water vapour changes to a cloud of droplets.[1] This can be described thermodynamically in terms of a function called the Gibbs Free Energy G, which is defined as

$$G = U - TS + pV,$$

where U is internal energy, T is absolute temperature, S is entropy, p is pressure, and V is volume. For a uniform system we can divide by the number of molecules involved, and the result μ is termed the chemical potential. It can be shown that for any closed system at constant pressure G tends to decrease towards a minimum value, and this provides a means for exploring the development of such systems.

So let us consider a uniform parcel of humid air with a water vapour pressure p which is greater than the saturated vapour pressure p_0 at the ambient temperature. It can be shown from the definition of G that the chemical potential for a water molecule in the vapour relative to that in liquid water at the same temperature is

$$\mu_V - \mu_L = kT \ln(p/p_0),$$

where k is the Boltzmann constant as usual. The free energy increase from formation of a water droplet of radius r from the vapour is therefore

$$\Delta G = -(4\pi/3)r^3 nkT \ln(p/p_0) + 4\pi r^2 \sigma$$

where n is the number of molecules per unit volume in water and σ is the surface free energy of water per unit area, which is the same as the surface tension for a liquid. When this expression is plotted as a function of radius for the case $p > p_0$ corresponding to supersaturated vapour, it has the form shown in Fig. 1 with a maximum ΔG^* at radius r^*.
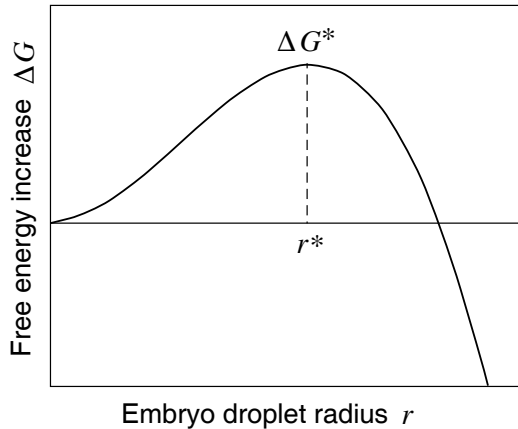
Figure 1. Free energy ΔG required for embryo droplet production as a function of droplet radius r. ΔG^* is the nucleation barrier.

In equilibrium there will be a population of extremely small sub-critical droplets in the vapour, but in order that stable droplet nucleation can occur, it is necessary to surmount the free energy barrier created by this maximum. The rate at which this occurs can be shown to be

$$J \sim 10^{25} \exp(-\Delta G^*/kT)$$

per cm^3 per second near normal atmospheric temperature. When values of the parameters are inserted it works out that an appreciable nucleation rate of say between 10^{-3} and 10^{+3} droplets per cm^3 per second requires a saturation ratio p/p_0 in the range 4.0 to 4.8. Such a high supersaturation is achieved only in equipment such as cloud chambers, while atmospheric supersaturation never exceeds a few percent. So how do droplets form?

The answer lies in nucleating particles. In a cloud chamber these are positive ions produced along the trails of the particles being tracked, while in the atmosphere they are tiny particles released from dust or sea-spray or industrial smoke.

Solid particles can act as condensation nuclei with a water droplet nucleated on the surface as shown in Figure 2. As well as the particle radius R, a very important parameter is the contact angle θ of water on the particle surface, defined by the force-balance relation

$$\sigma_{SV} = \sigma_{SL} + \sigma_{LV} \cos \theta$$

where σ_{AB} is the surface free energy or surface tension between A and B, with S implying the solid particle, L the liquid water, and V the surrounding vapour. Nucleation theory can be extended to cover this case, with the free-energy barrier ΔG^* then being a function of the particle radius R and the contact angle θ, or more conveniently of $m = \cos \theta$, as shown in Figure 3.

Since the supersaturation in typical clouds rarely exceeds 1%, it is clear that such solid particles need to have a very small contact angle and to be larger than about 200 nanometres in diameter if they are to have any role in cloud formation.
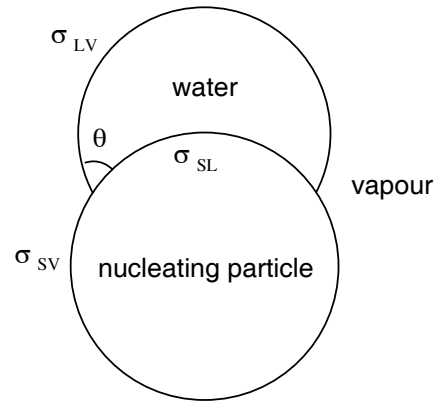

Figure 2. Nucleation of a water droplet on the surface of a solid particle. The contact angle is θ.

Soluble particles, however, are much more efficient nucleators, and work by forming small droplets of salt solution even when the surrounding vapour is not quite saturated. For a soluble particle as small as 100 nanometres, the equilibrium water droplet at saturation has a diameter rather larger than this and, most significantly, the barrier to droplet growth can be surmounted at a supersaturation of only a few tenths of one percent. Droplet growth is therefore almost an equilibrium process, with the larger soluble nuclei surmounting the barrier first and depleting the supersaturation so that the smaller nuclei are never activated above their barriers.
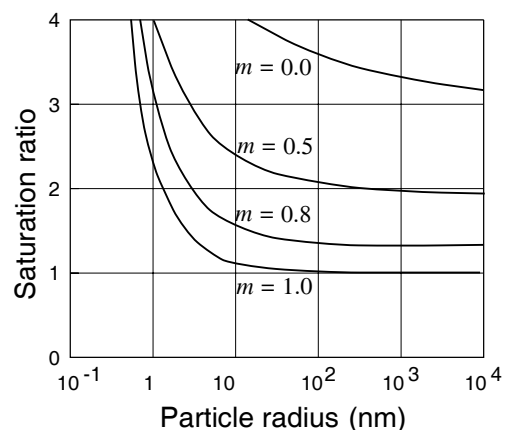

Figure 3. Critical saturation ratio for nucleation of a water droplet in one second[1] on a particle of radius R with a contact angle parameter $m = \cos \theta$.

The spectrum of droplet sizes in a cloud will therefore depend upon the size spectrum of the soluble nuclei

present and also to some extent upon the rate at which the air parcel is rising, which determines the rate of increase of supersaturation. Measurements on air masses of continental origin show large particle concentrations for diameters below about 100 nm and a rapid decline above this size, while maritime air masses have a much smaller and narrower distribution of particle diameters peaked around 1 μm.

The spectrum of cloud droplet sizes is generally of the "log-normal" type, with the logarithm of droplet diameters being normally distributed, giving the result shown in Figure 4. when plotted on a linear scale. The droplet concentration depends upon the type of cloud and the history of the air mass in which it grows. Clouds originating in warm tropical regions have greater liquid water content than clouds growing in cooler drier climates, the variation being from about 1 down to 0.3 g/m^3. The droplet concentrations also vary between about 50 per cm^3 for clouds growing over the sea up to as many as 2000 per cm^3 for continental cumulus clouds in times of drought. Since the water content is also generally lower in continental clouds, there is a corresponding large variation in mean droplet diameters, the peak in the distribution being observed to range from about 40 μm for maritime clouds down to about 10 μm for continental cumulus clouds.

Rain Formation by Coalescence

Since the air in a cloud is normally rising at a rate that ranges from about 1 m/s in a small cloud to more than 10 m/s in a large thunder cloud, the cloud droplets must fall against this updraft. But the terminal velocity of a water droplet reaches 1m/s only if its diameter exceeds 200 μm, and nearly all droplets are much smaller than this, so some sort of coalescence mechanism must be involved. One might think this was simply a matter of slightly larger droplets overtaking slightly smaller ones and colliding with them, but it turns out that droplets do not collide but avoid each other because of air viscosity unless one of them is larger than about 30μm in diameter. Coalescence efficiency then rises rapidly with collecting drop size.

Maritime clouds, or those produced from air masses that have moved for a considerable distance across an ocean, have relatively small concentrations of rather large droplets and can thus produce rainfall efficiently by a simple coalescence process. Clouds growing in continental air masses, on the other hand, particularly if these are loaded with dust or smoke, have very large numbers of very small droplets and these fail to coalesce to produce raindrops.
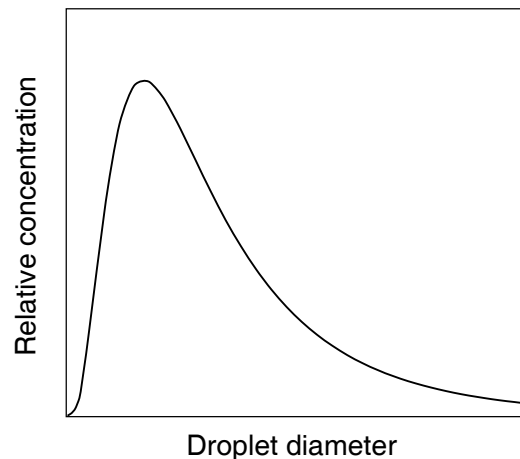

Figure 4. A log-normal distribution of cloud droplet diameters as plotted on a linear scale.

Raindrops must, of course, be able to fall against the cloud updraft if they are to reach the ground. The terminal velocity for a drop of radius r (in mm) increases about as 120 r^2 m/s for small drops but saturates at about 10 m/s for drops larger than about 4mm in diameter. Most raindrops are in the 1 to 3 mm range, and drops larger than 4 mm in diameter tend to break up under aerodynamic forces as they fall.

Freezing and Sublimation

If continental-type clouds cannot produce raindrops by coalescence of cloud droplets, then how do they rain at all? If you look at a large cumulus cloud then you will often see that the top looks different and tends to form an anvil plume that blows off to one side. This is a plume of ice crystals and, on reflection, it is not strange that they form, since the lapse rate should place the freezing level something like 2 km above the land surface, and large cumulus clouds can be very much taller than this. But again we encounter a nucleation problem: exactly how does a water droplet freeze?

The simple theory of homogeneous freezing[1] is very similar to that of homogeneous condensation except that instead of vapour supersaturation being the driving force it is now liquid supercooling. Suppose we have some liquid water at a temperature that is below the freezing point by an amount ΔT, then the chemical potential of the water molecules relative to those in solid ice could be expressed just as before in terms of vapour pressures, but is more conveniently written as

$$\mu_L - \mu_S \approx (L/n)\,\Delta T/T_0 \; ,$$

where L is the latent heat of melting of ice per unit volume, n is the number of water molecules per unit volume in ice, ΔT is the supercooling and T_0 is the melting temperature of ice. The problem now, rather as with homogeneous condensation, is that the

calculated nucleation temperature for freezing in a moderate sized droplet is about –45°C. Recognising that an ice crystal is not a sphere but a faceted structure makes things worse rather than better!
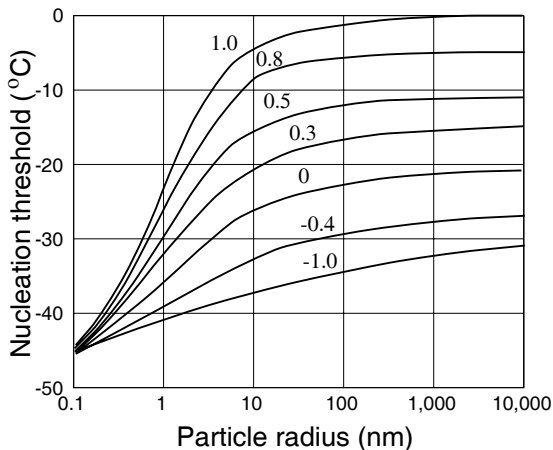

Figure 5. Calculated threshold temperature for nucleation of freezing of water[1] by a particle of radius r with contact parameter m.

Once again the solution lies in heterogeneous nucleation on foreign particles suspended in the water droplets and the crucial parameters are the particle size and the contact parameter $m = \cos\theta$, with θ determined from an equation similar to that used before but with appropriately altered subscripts. The calculated results are shown in Figure 5. To be effective at cloud temperatures, the particle must have a diameter greater than about 20nm.

Another possibility is that ice might nucleate directly from the vapour by sublimation onto the particle concerned. Again the analysis is similar to that for condensation, and when numbers are inserted we find the results shown in Figure 6. To be effective, nucleating particles must now be larger than about 200 nm in diameter and must have a contact parameter m, defined now in terms of ice and vapour, greater than about 0.9.

Once again the crystalline nature of the nucleating particle can be taken into account, but now it is crucial. Since the ice is growing epitaxially on the substrate, the energy of the interface and thus the value of the parameter m depends strongly on the crystalline lattice relations involved. To obtain the desired value of m close to unity requires minimisation of the energy of the ice/substrate interface, and this will be facilitated by a good crystalline structure match between these two materials.

Crystal interfaces have received a great deal of attention, particularly recently in relation to epitaxial growth of semiconductors, and the situation with ice,

investigated[1] about fifty years earlier, is very similar since the crystal structure of ice is the hexagonal analogue of the diamond cubic structure of common semiconductors. To obtain an interface with low energy requires a good match in geometry and lattice parameter between the nucleating particle and ice, and such a material was identified in the 1940s by Bernard Vonnegut to be silver iodide. The lattice geometry is the same as that of ice, and the lattice parameter mismatch on (0001) faces is only 1.3%. This gives an m value close to 1 and a nucleation temperature for large particles of about –4°C. Silver iodide remains the preferred nucleation material for cloud seeding up to the present day.

Of course, silver iodide does not occur naturally in the air, if only because it is rapidly decomposed to metallic silver and free iodine by sunlight, just like its photographic cousin silver bromide. But the same principles apply and, while natural minerals do not approach silver iodide in nucleation efficiency, many have nucleation thresholds around –15°C. Individual particles with pits or scratches or pairs of particles clumped together may have higher thresholds, and the abundance of such dust particles in the air, particularly continental air, ensures that most clouds develop ice crystals in their tops once they reach a temperature below about –15°C.
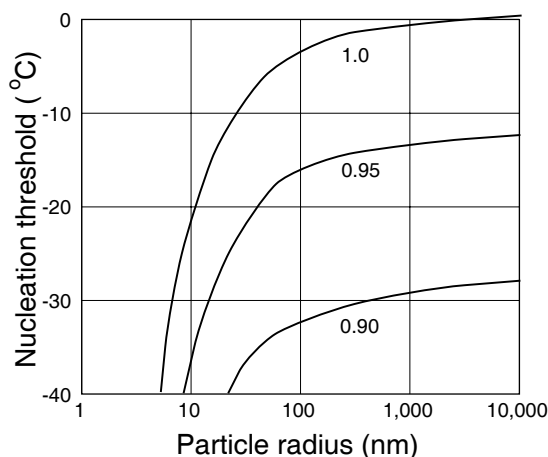

Figure 6. Calculated threshold temperature[1] for nucleation of ice sublimation by a particle of radius r with contact parameter m.

Once ice crystals have formed, they grow rapidly at the expense of the surrounding supercooled water droplets, because the vapour pressure over a supercooled water droplet is greater than that over an ice crystal. The snowflakes thus formed fall through the cloud and collide with cloud droplets which freeze on contact, forming grains of sleet or, if the water content is high, hailstones. These then melt when they fall below the freezing level and finally appear as

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raindrops. This melting transition is clearly visible as a bright band on radar because the dielectric constant of water is much greater than that of ice at microwave frequencies.

Industrial Pollution

It has been suggested by Daniel Rosenfeld of the Hebrew University of Jerusalem that, because smoke from industrial pollution changes the droplet concentrations in clouds, an effect that is visible from satellite studies, this can have a significant effect on rainfall downwind.

Rosenfeld's conclusions, not particularly those about Australia but those concerning other parts of the world, have excited considerable attention and dispute and the matter is still far from resolved. In general terms, however, it does seem reasonable that any form of atmospheric pollution can potentially have an effect on rainfall, though detailed study is required to discover whether this effect is significant, and indeed also whether it is positive or negative. The effect will certainly depend upon the chemical composition and size range of the particles released.

A report on a specific cloud-seeding proposal for Australia was prepared for the Department of the Environment and Heritage in 2002.[2] Since then Rosenfeld has published details of the studies on which the proposal was based,[3] information that was not made available at the time by his Australian commercial collaborator.

Rainmaking

If human activities are causing a reduction of rainfall in areas where water is in short supply, then the next question is what to do about it. Much the same question must be asked in relation to rainfall changes that are associated with natural or long-term variations in climate and weather patterns.

Physical understanding suggests that there are basically two options for increasing the rainfall from clouds: (i) add large salt particles (by which we mean a few micrometres) below cloud base to initiate nucleation and produce a reasonable concentration of large droplets before the small ones can form, or (ii) introduce efficient freezing of sublimation nuclei to produce ice crystals not too far above the freezing level. Both these possibilities have been tried and found to work at a reasonable level in individual clouds. In early experiments, condensation nuclei were distributed by spraying sea-water from an aircraft flying just below cloud level, or ice crystals were produced by dropping pellets of dry ice from an aircraft flying above the cloud tops. More recently silver iodide smoke, produced by dissolving silver iodide in acetone with the aid of an potassium iodide co-solvent and releasing smoke from the burning solution from an aircraft flying through the cloud near the freezing level, has become a standard method in many places. In other cases, as will be discussed below, the silver iodide smoke may be released into the cloud from burners at ground level and carried up by the updraft. There has also been some renewed interest in a process involving spraying of liquid CO_2 into the cloud from an aircraft flying just above the freezing level.

But the actual seeding technique is not the whole story. For a cloud seeding program to be effective it needs to be economically viable over an adequately large area and, because of the large variation in weather and cloud patterns, it needs to be evaluated statistically with appropriate controls over a long period. This has usually been done in one of several ways. One is to set up the cloud-seeding system and then, on each day or perhaps each week, toss a coin to decide whether it is to operate or not and then compare seeded to un-seeded periods. To make this even better, it should be done on a "double-blind" basis with neither the operator nor the analyst knowing which periods were seeded and which were un-seeded, for example by having a concealed and coded switch on the silver-iodide supply to the burner.

Many variations of this scheme are possible, for example by having two neighbouring areas with similar rainfall patterns and seeding either one or the other on a random basis.

There is a possible problem with these procedures, however, in that the seeding agent may perhaps remain in the area for a considerable time, for example upon the leaves of trees, thereby causing initially promising results to decrease in significance as time progresses. This appears to have happened in some cases.

Cloud seeding has been in operation in Australia since it was begun on an experimental basis by CSIRO in the early 1950s. One of the most promising areas has been the tablelands of Tasmania, where any increases in rainfall has large commercial value since the water is used for hydroelectric power generation. This program continued and is still in operation, the latest analysis confirming an average 8% increase in rainfall in the target area and no detectable decrease in downwind areas. A similar program was operated in the 1960s in the Snowy Mountains of New South Wales, where again the rainfall is of high commercial value. The results at the time were controversial so the program was not continued on an operational basis, but about four years ago another program was launched in the area with improved methods of analysis and is currently in operation.

Current Australian programs use ground-based seeding in mountainous areas where the smoke is carried efficiently up into the clouds. This is a much less expensive procedure than using aircraft, but some programs in Texas in the USA are based upon targeting individual cloud areas using radar and despatching aircraft for selective seeding. This may be a more efficient way to proceed from a seeding point of view but it is much more expensive, and this must be taken into account. The same is true of attempting seeding operations over widespread areas of relatively flat agricultural land, where ground-based seeding may not be very effective and the commercial value of added rainfall is lower.

There is, in some areas, the possibility of an adverse effect from cloud seeding with silver iodide smoke. This can occur when, for some reason, the clouds already contain adequate ice-forming nuclei so that their tops are already glaciated. If large additional concentrations of freezing or sublimation nuclei are added, then the result may be that very large concentrations of very small ice crystals are produced, leading to a problem similar to that of coalescence in continental cumuli and a consequent possible reduction in rainfall. Such an effect could, however, be expected to be associated with air masses coming from particular directions, and the cloud-seeding procedures could be modified to take account of this. Something of this nature was found in a recent analysis of the long-term results of the Tasmanian cloud-seeding project, where precipitation from clouds in air masses coming from some particular directions was significantly increased while that from air masses from some other directions was not. Analysis of the Tasmanian experiment also showed no depletion of rainfall in areas downwind of the seeded regions.

My conclusion is that cloud seeding using silver iodide is an appropriate technique to apply in areas where the value of the rainfall is high and where preliminary experiments have demonstrated that it works.

Some people have expressed queries about the possible danger of dispersing silver iodide nanoparticles in the atmosphere, particularly when they end up in water supplies. There do not, however, appear to be any grounds for concern. The amount of silver iodide dispersed is extremely small — less than one part in ten billion in the resulting raindrops — and within a few hours it is converted to metallic silver by the action of sunlight. The co-solvent material, potassium iodide, also readily disappears since it is soluble in water and is also in minute quantities in the rainfall. It constitutes no hazard.

Cloud Seeding and Pollution

The other area that is presently under attention is the use of cloud seeding techniques to reduce the possible adverse effect of industrial pollution on rainfall in downwind areas. The suggestions that have been made range from seeding clouds with silver iodide released either from aircraft or ground-based burners to similar seeding efforts using salt water to introduce large hygroscopic particles.

My view on this matter is that, while cloud seeding might help to alleviate the effects of industrial and other pollution, it is probably not the way to proceed in the Australian situation. Here most of the major pollution sources are large coal-burning power plants, so that the sources are localised and clearly identifiable. Rather than trying to overcome the problem by seeding clouds far downwind, the obvious remedy seems to be either to reduce the emissions at the source, or else to inject suitable concentrations of salt particles into the chimney exhausts, perhaps by using sprays of sea water. The matter is still under discussion.

Conclusions

The behaviour of clouds is a mixture of phenomena at all scales from mega to nano. Humans can have influence over the long term at the kilometre stage through land and water management, but one of the most promising fields involves use of nanoparticle technology to influence the behaviour of cloud droplets which are themselves in the micrometre domain.

The field has now been under development for about sixty years, but results and predictions remain controversial. Part of the reason for this is that every region of the world is different, and what works well in one place may be ineffective in another. The only way to discover is to try experiments, which must be both well designed and extended in time if they are to produce reliable results.

References

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2. N.H. Fletcher *Advice on the Impact of Pollution on Rainfall and the Potential Benefits of Cloud Seeding* (December 2002)

3. D. Rosenfeld, I.M. Lensky, J. Peterson and A. Gingis "Potential impacts of air pollution aerosols on precipitation in Australia" (2006) *available on the web site* http://www.earth.huji.ac.il/staff-main.asp?id=149