

# The algae-cloud connection

Cape Grim, on Tasmania's north-western coast, where atmospheric constituents are monitored.

Clouds may be largely water, but a vital ingredient is sulfur. Without it the constituent water droplets would have very few seed particles, or nuclei, to grow around.

Wherever in the world scientists sample air, over land or ocean, the particles they find frequently contain this element. Sulfuric acid particles are the most common; others are usually ammonium bisulfate or ammonium sulfate.

Over land, most of the sulfur-containing particles that act as cloud nuclei come from man's burning of oil and coal, the smelting of sulfide ores, and so on.

But strangely, even in the most remote localities — such as over the southern oceans — scientists find that each cubic centimetre of air typically contains hundreds of submicroscopic sulfur-containing particles capable of inducing water droplets to form.

Naturally occurring sulfur compounds they have detected include sulfur dioxide,

hydrogen sulfide, carbon disulfide, carbonyl sulfide, methanesulfonate, dimethyl sulfide, and dimethyl disulfide.

Where does all this natural sulfur come from? It's an important question, for it sheds light on the difficult question of what effect civilization's prolific liberation of sulfur during combustion may be having on cloud formation.

In the Northern Hemisphere sulfur from man-made sources exceeds the quantity from natural sulfur sources. This extra contribution could be expected to alter cloud and rainfall patterns from those existing when industrialization began apace last century, but detailed meteorological records don't go back far enough to show definitely whether this has happened. The evidence does show that, if changes have occurred, they haven't been drastic.

## Tracking it down

The sulfur in remote localities hasn't got there by long-distance transport from populated centres where fossil fuels are burnt.

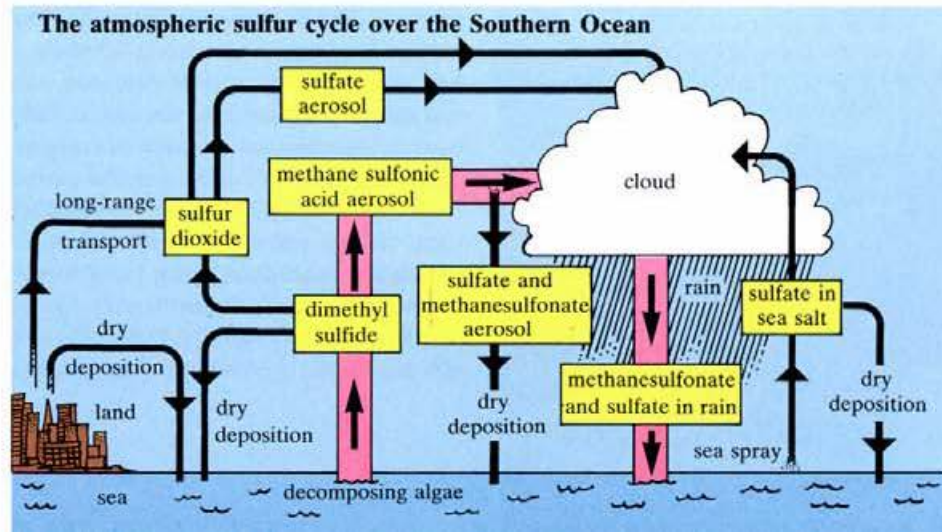
As the 'acid rain' problem has shown, the offending sulfur dioxide released from smoke stacks is very soluble, and soon dissolves in clouds and rains out. Most will have been removed from the atmosphere within about 1000 km from where the gas is released.

Where the sulfur dioxide drifts out over the sea, it is even more rapidly depleted, since ocean waters are alkaline and quickly absorb the gas into the surface layers.

Yet even in remote parts of the Southern Hemisphere, as far as you can get from civilization, sulfur dioxide at 50–100 parts per million million (p.p.m.m.) can be detected. Scientific analysis also reveals sulfur compounds in the purest of rain-water, and particles of sulfuric acid and ammonium sulfate in the cleanest air.

## Rotting seaweed contributes to cloud-droplet nuclei.

**A major pathway (red) links cloud formation with algae in the sea. Decomposing algae produce dimethyl sulfide gas, which turns into particles of methane sulfonic acid, which provide nuclei for cloud droplets to form around.**



A proportion of the sulfur comes from the sulfates in sea water, which become airborne when sea spray evaporates. This process accounts for about two-thirds of the estimated 100 million tonnes of sulfur derived from natural sources that rain down out of the skies each year. But, as we shall see, this proportion doesn't account for the majority (in numbers) of sulfur particles in the air. The particles derived from sea spray are relatively large and heavy, whereas most of the airborne particles scientists detect are tiny ( $0.1\text{ }\mu\text{m}$  in diameter, or less).

Studies by two scientists from the CSIRO Division of Atmospheric Research have strengthened the supposition that, apart from that originating in sea spray, most natural sulfur derives from dimethyl sulfide — a smelly gas that rises into the air from decomposing sea plants.

Dimethyl sulfide wasn't even recognized as an atmospheric constituent until a decade ago. We now know that in clean air it provides the source of sulfur from which most of the small airborne particles are created.

Recently, some American scientists measured the concentration of dimethyl sulfide in sea-water samples from around the world, and found it dissolved there in consistently appreciable quantities. They estimated that, on a global scale, it totals enough to diffuse into the atmosphere in quantities that roughly balance the amount of natural sulfur (minus that from sea spray) returned to earth in rain.

The work of the CSIRO scientists, Dr Keith Bigg and Dr Greg Ayers, confirms the important role of dimethyl sulfide in the natural sulfur cycle.

### Sensitive instruments

Dr Bigg's main interest has been studying the origin of the tiny cloud-droplet nuclei.

### High-volume air-sampling equipment on the roof of the Cape Grim observatory.



He concludes that in remote areas most are produced from the action of sunlight on this dimethyl sulfide.

Dr Ayers' scientific investigations have centred around atmospheric chemistry, and his studies lead him to think that dimethyl sulfide is a significant natural source of rain-water acidity.

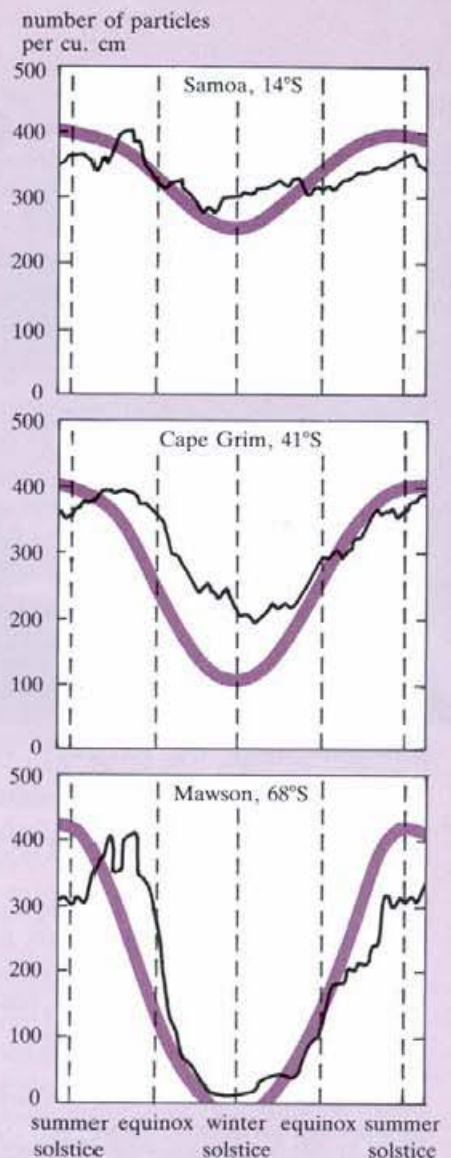
Instruments operating in the clean air of the Australian Baseline Air Pollution Station at Cape Grim, Tasmania, have been a major source of data for both researchers.

Dr Ayers, with the assistance of Mr John Ivey of the Australian Government Analytical Laboratories in Hobart and Mrs Helen Goodman of the Division, analysed the airborne material trapped in Cape Grim's high-volume air filters. He used ion chromatography to look for methanesulfonate, since laboratory studies indicated that this aerosol should be produced from the breakdown of dimethyl sulfide gas, and traces of the substance had been detected in air at Hawaii.

Dr Ayers' analysis produced positive results, although the quantities of methanesulfonate detected on each of the filters were minute — averaging only 18 nanograms per cubic metre of air. Thus, many thousands of cubic metres of air had to be filtered to obtain enough for reliable measurement. Despite the very small quantities involved, they are a clear indication of dimethyl sulfide at work.

Although, over the ocean at least, the predominant mass of airborne particles comes from relatively large salt particles, in terms of numbers the tiny sulfur-containing particles ('Aitken' particles) are the most abundant. The number of particles is crucial in determining the number of droplets per unit volume of cloud, and this in turn has a strong bearing on the cloud's persistence, the amount of solar radiation it reflects back to space, and the likelihood of rain.

(Of course, the number of ice crystals in a cloud is another factor that is very



**How light influences particle numbers**

The number of particles observed at each station (black curve) follows the amount of sunlight each receives (colour), and Dr Bigg thinks this is because the particles originate from a photochemical reaction. Phase differences between the two curves reflect the half-life of the particles.

important in producing rain — artificial cloud seeding aims at inducing rain by increasing ice crystal abundance. In most clouds, water-droplet nuclei outnumber ice-crystal nuclei by thousands, if not millions, to one.)

Dr Bigg has operated an aerosol particle counter at Cape Grim for a number of years. It detects the scattering of light by particles in the path of a strong light beam, and on occasions it has provided circumstantial evidence that dimethyl sulfide from the oceans is the source of many of the particles needed for cloud formation. He's observed that, whenever the smell of Cape Grim's rotting seaweed strikes his nostrils, the particle counter has shown a big increase in aerosol numbers!

A closer investigation revealed that air upwind of the beached seaweed had a

particle concentration of about 200 per cu. cm, whereas the corresponding figure downwind was some 20 000 per cu. cm. This nicely corroborates an observation made in 1910 by Dr John Aitken — after whom atmospheric aerosols are named. He noted that wind blowing over a Scottish seashore picked up extra particles.

### Seasonal variations

Dr Bigg and two colleagues, Dr John Gras and Mrs Christine Evans, have now shown that particle numbers in remote areas of the Southern Hemisphere vary with the seasonal availability of sunlight. This variation provides strong evidence that dimethyl sulfide is the main particle progenitor, says Dr Bigg, since chemists have shown that light promotes the transformation of the gas into methanesulfonate aerosol.

Dr Ayers also finds a seasonal variation in methanesulfonate concentrations in the air, but he attributes it to changes in the abundance of seaweed and phytoplankton according to season. His data show variations as great as tenfold — much more than the change in sunlight from summer to winter at Cape Grim. A similar kind of variation showed up when Mr Ivey and Dr Ayers analysed rain-water collected at the Cape for methanesulfonate. (Indeed, since they began looking for it, the compound has turned up in rain-water samples from numerous places around Australia, and in Antarctic snow and ice as well.)

Be that as it may, Dr Bigg's particle counter at Cape Grim shows a twofold variation from summer to winter — close to the change in the quantity of light between the seasons. In addition, particle numbers at five other remote stations — at different latitudes — show variations that parallel the way in which the sun's intensity varies at that latitude.

For example, at Samoa, near the Equator, there is not much of a seasonal effect, but near the South Pole the particle numbers at three Antarctic bases fell almost to zero during the long winter night.

The observed yearly cycle in particle numbers cannot be explained by spray or bubbles from the ocean surface. It would also be very difficult to account for the observations by assuming that particles are transported from continents in such a systematic way. (Cities are major sources of particles, principally from combustion.)

Indeed, from studies of particles transported from Sydney, Melbourne, Adelaide, and Perth to Tasmania (and sometimes to New Zealand), Dr Bigg calculates that airborne particles decrease in number by

about two-thirds for every 1000 km travelled. So by the time our civilization's air reached Samoa or Antarctica, the enhancement would be negligible.

### Delayed response

When Dr Bigg looked closely at the way particle numbers varied, it was apparent that, at all the stations, the time of minimum particle numbers did not correspond exactly with the winter solstice. The explanation is that it takes some time for particle numbers to fall in response to the diminishing light; readings from the South Pole stations suggest that it takes about 30 days for half the particles to disappear there. As this is the value commonly quoted for the half-life of particles in the upper troposphere, the figures support the notion that a photochemical process produces the particles.

Cape Grim data also reflect a 30-day particle half-life. This could be viewed as an inconsistency, in that winter showers fall so frequently there that you might expect airborne particles to be quickly washed out. However, Dr Bigg suggests that particles produced above the cloud tops form a reservoir that promptly replenishes the lower atmosphere after rain.

To check this theory, he arranged a score of aircraft flights to 3000 m above Cape Grim. The particle counter on board the plane showed a significant correlation between the number of surface particles and the number higher up.

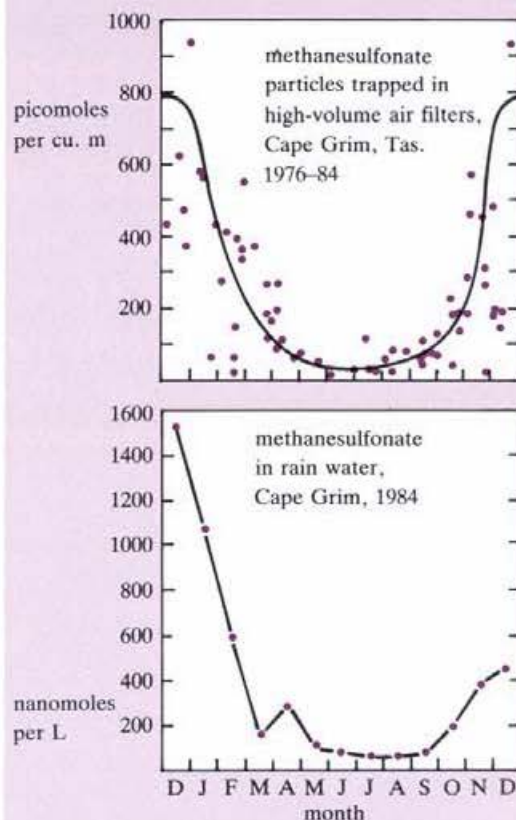
Laboratory studies have demonstrated that dimethyl sulfide can give rise to sulfur dioxide and particles of sulfate (most commonly sulfuric acid or ammonium sulfate), as well as methanesulfonate.

So if dimethyl sulfide is breaking down to give methanesulfonate, we should also expect to see quantities of these other substances. As mentioned earlier, clean maritime air always contains at least 50 p.p.m.m. of sulfur dioxide, and Dr Ayers and Mr Ivey have isolated amounts of

**Although dimethyl sulfide is not the most abundant sulfur compound in the air, scientists think it is the most important one for the turnover of the element in the natural sulfur cycle. It is very reactive and quickly turns into other compounds, most notably into particles of sulfate and methanesulfonate.**

#### Natural sulfur-containing gases

		typical concentration (parts per million million)
dimethyl sulfide	$\text{CH}_3\text{SCH}_3$	60
sulfur dioxide	$\text{SO}_2$	75
hydrogen sulfide	$\text{H}_2\text{S}$	30
carbonyl sulfide	$\text{OCS}$	500
carbon disulfide	$\text{CS}_2$	15



Annual cycles in sulfur

**Dimethyl sulfide gas from the ocean breaks down into particles of methanesulfonate once in the air. Dr Ayers finds an annual cycle in the particulate's abundance, and sees this as evidence of its algal origin.**

sulfate in excess of that derived from sea salts.

They could distinguish sulfate of marine origin by looking at the level of magnesium. The ocean has a fixed ratio of magnesium to sulfate. Any sulfate in excess of this ratio must have come from atmospheric reactions, and they measured this 'excess' sulfate from the high-volume filters at Cape Grim at 0.3 µg per cu. m.

Dr Ayers is convinced that the excess sulfate originates from ubiquitous dimethyl sulfide. However, he is puzzled that this excess shows no apparent seasonal cycle, unlike its sibling, methanesulfonate.

We still have a good deal to learn about Nature's sulfur cycle, but at least we now know that cloud formation is related to rotting seaweed.

Andrew Bell

### More about the topic

Origin of Aitken particles in remote regions of the Southern Hemisphere. E.K. Bigg, J.L. Gras, and Christine Evans. *Journal of Atmospheric Chemistry*, 1984, 1, 203-14.

Sulfate and methanesulfonate in the maritime aerosol at Cape Grim, Tasmania. G.P. Ayers, J.P. Ivey, and H.S. Goodman. *Journal of Atmospheric Chemistry*, 1986, 3 (in press).