Iodine's air of importance

Charles E. Kolb

Iodine-containing emissions from marine algae can be converted by sunlight into aerosol particles. If this phenomenon occurs on a large scale, it could have significant effects on climate.

The discovery of a previously unrecognized source of aerosol particles is big news to atmospheric scientists. Just such a source is described by O'Dowd *et al.* on page 632 of this issue[1]. Building on earlier work, they have unravelled a photochemical phenomenon that occurs in sea air and produces aerosol particles composed largely of iodine oxides. The precursor molecules are organic iodide vapours emitted by marine algae.

One reason for the interest in atmospheric aerosols is their effect on climate and on our understanding of climate change[2]. In particular, uncertainties about the composition and distribution of fine aerosol particles, no more than a few micrometres in diameter, cause large uncertainties in predictions of global warning driven by the accumulation of greenhouse gases. Depending on their composition, aerosols can have a direct effect on Earth's radiative balance by back-scattering (or absorbing) incoming solar radiation, leading to cooling (or warming). Indirectly, their influence is felt through their action as cloud-condensation nuclei, catalysing cloud formation. The more aerosol particles that can induce droplet formation in a cooling air mass, the smaller the resulting cloud droplets. Smaller droplets produce brighter clouds, which might also be longer lived because they are less likely to precipitate as rainfall. Indeed certain observations indicate that aerosols from forest fires and urban pollution can suppress rain and snow fall[3,4].

Aerosol sources are shown in Fig. 1 and can be divided into two types. Primary aerosols are emitted directly, such as smoke from bush or forest fires, soot and ash from factories, motor vehicles, trains, boats and planes, airborne dust, and sea-salt particles produced when sea spray dries out. Globally, however, much of the ambient particulate burden, and most of the fine aerosols, are produced in the atmosphere itself. These secondary aerosols arise from oxidation of precursor gases, such as sulphur dioxide, nitrogen oxides and volatile organic compounds, to form less volatile products. The resulting oxidation products then nucleate to form new particles or condense on pre-existing particles. Figure 1 also indicates the main effects of atmospheric particles.

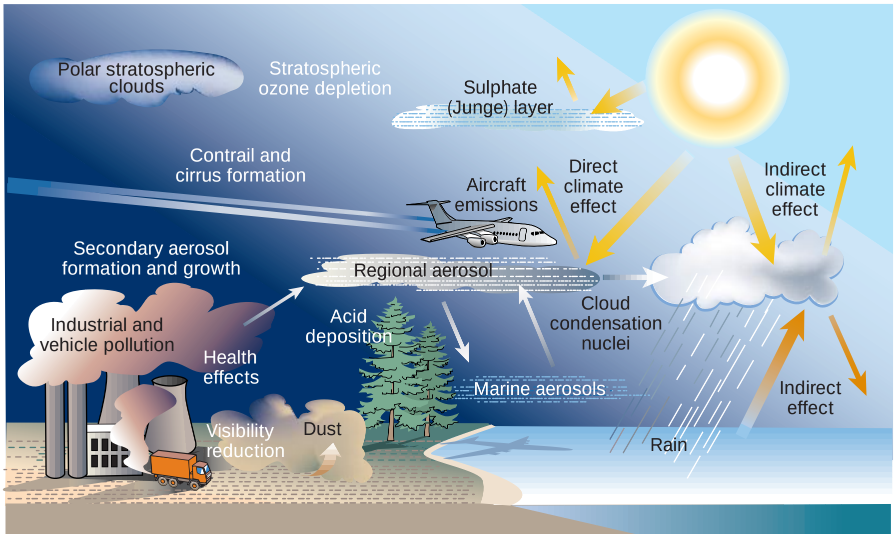

Figure 1 **Aerosols — the big picture. Industrial and vehicle exhaust emissions, windblown dust, and salt from dried sea spray are all sources of primary aerosol particles. Secondary aerosol particles are produced in the atmosphere from gaseous pollutants in exhaust emissions, and emissions from land vegetation and marine organisms. Photochemical processes in urban smog produce high levels of secondary particles; lower, but still significant, levels stem from similar processes higher in the atmosphere. Atmospheric particles have many effects. Reactions catalysed in polar stratospheric clouds, and in the lower-latitude stratospheric sulphate (Junge) layer, result in ozone depletion. Photochemically produced particles of sulphuric acid, and nitric acid, lead to acid deposition. Fine aerosol particles of both primary and secondary origins can affect human health, reduce visibility, and influence climate both directly and indirectly. Particles and precursor gases emitted by aircraft in the upper troposphere and stratosphere can have a disproportionate effect because these regions are not heavily polluted by ground-level emissions. The mechanism discussed by O'Dowd *et al.*[1] might be an important contributor to the marine aerosol layer, and especially the tropospheric layer immediately above: sea-salt aerosols are fairly large and are generally not transported far above the surface.**

For many years it was assumed that the primary chemical source of new atmospheric particles was the co-condensation of sulphuric acid vapour and water vapour[5]. Over continental areas, sulphuric acid vapour is formed primarily by the oxidation of sulphur dioxide produced in burning oil and coal. In clean marine environments it is produced by the oxidation of dimethylsulphide and other reduced sulphur compounds emitted by marine organisms[6].

With improved measurement techniques, however, bursts of formation of new particles have been observed when the concentration of sulphuric acid vapour is too low to support its combination with water vapour. In some special cases, atmospheric concentrations of other condensable inorganic species, for instance ammonia or nitric acid vapour, are high enough to account for particle formation and growth through a nucleation mechanism[7]. And quite recently, evidence has emerged for a completely different source in forested regions: gaseous monoterpenes released from trees can be photo-oxidized to condensable carboxylic acids fast enough to produce bursts of particle formation and growth[8,9].

Over the past few years, O'Dowd and co-workers have observed episodes of particle creation in their study areas along the Irish coast. But these episodes could not be explained by nucleation and condensation driven by sulphuric acid or carboxylic acids[10–12]. Knowing that seaweed can emit easily photolysed alkyl iodide compounds, such as CH_2I_2, and that the resulting gaseous iodine reacts rapidly with ozone and other atmospheric oxidants to produce iodine oxides, they explored this avenue through laboratory experiments. This preliminary research showed that the photolysis of CH_2I_2 in the presence of ozone produces copious numbers of fine particles[13].

In their latest paper[1], O'Dowd and colleagues have taken the earlier work a crucial step further. They have extended the laboratory experiments to realistic coastal conditions, reproduced in a state-of-the-art atmospheric smog chamber. They show that the photolysis of CH_2I_2 at concentrations as low as 0.015 parts per billion by volume, well within levels often found in coastal environments, is a potent source of aerosol particles. Using a suite of instruments for characterizing the dynamics of particle formation and growth, and an aerosol mass spectrometer for determining chemical content as a function of particle size, they charted particle dynamics and confirmed that the particles formed in their chamber were predominantly composed of iodine oxides, the simplest of which may be OIO, HOI and I_2O_2. The authors' suggested reaction mechanism for the creation of these species, after the photochemical production of iodine from algal CH_2I_2 emissions, is shown in their Fig. 2 on page 633.

To produce stable new particles in the clean, open-ocean marine atmosphere, concentrations of condensable vapour have to be high enough both to nucleate new nanometre-scale particles and to allow them to grow by agglomeration and vapour condensation to the stable 50–100-nm size range[5]. If there is too little condensable vapour, new particles don't form or they re-evaporate or agglomerate with pre-existing particles. O'Dowd *et al.*[1] describe modelling calculations which suggest that CH_2I_2 concentrations over the open ocean might well be high enough for the resulting condensable iodine oxides to allow newly nucleated sulphuric acid particles to become large enough to survive. The authors propose that the resulting particles might be abundant enough to influence the Earth's radiative balance. At the least, their model suggests that iodine oxides produced from volatile organic iodide compounds such as CH_2I_2 must be added to the list of precursors for secondary aerosol formation.

In retrospect, this might not be too surprising. In pioneering research off Hawaii[14] and Puerto Rico[15] in the 1970s, it was shown that iodine becomes concentrated in atmospherically processed sea-salt aerosol. In contrast, other halogens — chlorine and bromine — are depleted. These 30-year-old studies further showed that the iodine levels vary inversely with particle size, just as one would expect from a gas-phase condensable source of iodine oxide such as that described by O'Dowd *et al.*[1].

The obvious task that remains is to determine just how widespread this newly identified mechanism of particle growth is. To have a significant influence on climate, it would have to be effective over the oceans as a whole, not just in the coastal environment. The appropriate field-measurement tools and analytical models are already in hand. ■

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Developmental genetics

Buffer zone

Massimo Pigliucci

Heat-shock proteins help to protect organisms from external stresses. The idea that they can also buffer against internal — genetic — variations has received support from studies of fruitflies and, now, of plants.

Living organisms are caught between a hammer and an anvil, evolutionarily speaking. On the one hand, they need to buffer the influences of genetic mutations and environmental stresses if they are to develop normally and maintain a coherent and functional form. On the other, stabilizing one's development too much may mean not being able to respond at all to changes in the environment and starting down the primrose path to extinction. On page 618 of this issue, Queitsch *et al.*[1] propose that, in plants, the balance between stability and the potential for change is made possible in part through a protein involved in 'heat-shock responses' in a wide variety of species, from plants to insects.

Heat-shock responses are a fundamental and widespread type of cellular defence against environmental stress. They have been studied for their effects on the fitness of organisms[2]; for their co-evolution with other cellular functions[3]; for their role in response to stresses not related to temperature[4]; and for the level of natural variation in the genes that encode the heat-shock proteins (Hsps)[5], which mediate heat-shock responses. Notwithstanding the continuing debate[6] about the actual function of these proteins, it is now clear that they are a complex family of gene products that are involved in protecting other proteins. Some Hsps are expressed continuously in the organism, whereas others are triggered by several environmentally harsh conditions (not only increases in temperature).

Given the ubiquity of these proteins and their role in protecting organisms from environmental changes, it makes sense to ask a more subtle question: can they also help to protect against disruptive genetic variations? After all, the systems that allow organisms to develop from a fertilized egg to the adult form have been honed over millions of years of evolution, and it is likely that a mutation in any of the tens of thousands of genes involved would disrupt the entire process, just as a severe environmental stress does. This idea is rooted in the 1940s, in Waddington's classic studies[7,8] of 'canalization' — the resistance of developing organisms to change when perturbed genetically or environmentally. More recently it has been suggested that, from the point of view of development, internal disturbances are simply another form of environmental change that needs to be properly 'canalized' to maintain a viable form (phenotype) tailored to specific functions[9].

So can the Hsp proteins buffer genetic as well as environmental change? Rutherford and Lindquist[10] first tested the idea of a connection between Hsp activity and genetic variation by looking at a popular animal model of developmental genetics — the fruitfly *Drosophila melanogaster*. The results were stunning. When the authors disrupted Hsp90, by either mutating or inhibiting it, phenotypic variation in nearly every structure of adult *D. melanogaster* ensued, with the details depending on the genetic background of the insects used (that is, on which other specific genes were present in each individual). This led the authors to conclude that *D. melanogaster* accumulates hidden genetic variation, which is somehow kept by Hsp90 from affecting the phenotype. If the function of Hsp90 is partly compromised, the buffer breaks and we can see previously 'unavailable' phenotypic variants.

Queitsch, Sangster and Lindquist[1] have now expanded this research to another model of developmental genetics, the plant *Arabidopsis thaliana*[11,12]. These two species, *D. melanogaster* and *A. thaliana*, are of course very different in many ways. They have evolved separately over hundreds of millions of years. As one is a plant and the other an animal, they develop radically differently. And their breeding systems are not at all alike: fruit flies are obligatory 'outcrossers', meaning that they need a partner to produce offspring, whereas *A. thaliana* is mostly a 'selfer' — it fertilizes its own female gametes. Nonetheless, in *A. thaliana*, as in *D. melanogaster*, changes in Hsp90 release