Opinion

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Climate change: the effect of DMS emissions

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Environmental context. The idea that gases produced by plankton living in the oceans can affect cloudiness and regulate climate was given prominence by the promulgation more than 20 years ago by Charlson, Lovelock, Andreae and Warren of the CLAW hypothesis. In the intervening period it has been difficult to prove or disprove the idea, although much research has flowed from its enunciation. Perhaps its lasting legacy is in the way we view the planet and how research is conducted to try to understand how it operates.

The CLAW hypothesis^[1] came about almost by accident in 1985 during a visit by one of us. JEL, to the University of Washington in Seattle. It happened during a discussion with Robert Charlson about the role of clouds and dimethyl sulfide (DMS) in the Earth's climate. A paper by Shaw^[2] a few years earlier had first raised the possibility that the Earth's radiation balance could be changed by the reflection or absorption of solar radiation from clouds seeded by nuclei, the oxidation products of sulfur gases emitted by the oceanic biota. In the paper describing the CLAW hypothesis the authors also postulated that changes in the heat radiation flux would affect ocean surface temperatures and consequently algal growth and the emission of sulfur gases from the ocean surface. The feedbacks from this coupled system could either be stabilising, i.e. negative, or destabilising, positive. The emission of DMS and other sulfur gases from the ocean surface is now a well founded fact of observation,^[3–5] as is the oxidation of DMS^[6,7] in the atmosphere to become the source of sulfuric and methane sulfonic acids. Similarly there is little doubt that these products of DMS oxidation form a poorly quantified part of the population of cloud condensation nuclei (CCN), and that some of the cloudiness of the atmosphere is a result of algal growth in the ocean. What is hypothetical is the sign of the feedback on

climate, or even its existence, and the extent to which it plays any part in the present day climate.

In 1986, neo-Darwinist biologists found the notion that organisms were in any way involved in planetary self regulation, or altruism on a global scale, almost as objectionable as they now find evolution by intelligent design, see for example Richard Dawkin's book, The Extended Phenotype. It was not long before the CLAW hypothesis was subject to vigorous attempts at falsification. By great contrast climate scientists were so pleased to read anything that bore on the complex and unfathomable connection between clouds and climate that they welcomed the paper with enthusiasm, and the CLAW authors were presented with the Norbert Gerbier Prize of the World Meteorological Organization (WMO) in 1987. It is a measure of the near pathological isolation of the separated scientific disciplines that such different responses could happen.

Despite the lively reception of the hypothesis, there was in the late 1980s no direct evidence for it as a real world climate phenomenon. In the 1990s many measurements were made of the abundance of DMS, CCN, cloud density, air and surface water temperatures. None of these provided either strong support or convincing denial of the hypothesis. It was not until quite recently



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that Wolff et al.^[8] gave evidence from an ice core against CLAW and Vallina and Simó,^[9] Vallina et al.^[10] and Meskhidze and Nenes,^[11] substantial support. In the case of Meskhidze and Nenes, the strong link they report between marine biological activity and cloud properties is attributed to emission of isoprene, although the effect is much more likely to be a result of DMS, possibly in combination with other gases. A recent modelling study by Cropp et al.^[12] also adds strong support.

It would seem that all of the components of a CLAW mechanism are there so why is it so difficult to confirm? Maybe it's just too complicated to be subjected to simplistic tests. Naturally, being involved in its origin we are reluctant to see it forgotten. Could it be that we are looking for it at the wrong time? At present only 23% of atmospheric sulfur emissions are biogenic even though organisms in the ocean provide 42% of atmospheric column burden because of the longer lifetime of DMS compared with SO₂.^[13] In this connection failures to find evidence for CLAW may have been because many of the observations were made mainly in the much polluted northern hemisphere, where to seek the smaller biological effect would be like looking for butterflies in a fog. The apparent confirmation reported in the recent studies mentioned above was found in clean marine air, particularly in the southern hemisphere. In addition, Bates et al.^[14] show that in recent times in the southern hemisphere the dominant source of atmospheric S is biogenic, whereas for the northern hemisphere it is anthropogenic.

If this is correct it would seem that the CLAW effect is unimportant in the climate change now in progress, except perhaps in the southern hemisphere. We would speculate that it might have played a larger role in climate regulation during the glaciations when the oceans were cooler and algal growth favoured. This idea was explored and made the subject of a simple zero dimensional model by Lovelock and Kump.^[15] The model also had two stable climate states; one hot, when the CLAW effect was absent, and one cold, when it enabled the ocean biota to dominate regulation. This model prediction fits better with the Earth's past climate history than do the more usual geophysical climate models that have no stable hot state.

A powerful message from CLAW is that we should be looking for links between ocean plankton and atmospheric properties, both with respect to climate^[11] and air quality. There are many other gases emitted by the oceans in addition to DMS, e.g. alkyl nitrates, several organohalogens, NH₃, oxygenated organics, as well as biogenic particles.^[16] It is perhaps naïve to think that one gas acting alone (e.g. DMS) is responsible for particle formation; it is much more likely that a cocktail is involved. Many of these gases also play potentially important roles in air quality, particularly halogens in ozone destruction.^[17]

To end this piece we cannot do better than quote verbatim an anonymous reviewer of it – 'Even if CLAW turns out to be utterly irrelevant climatically, it will leave a rich and fundamentally important legacy in our perceptions of how the world works and in the way we need to do our science in order to understand it'.

References

 R. J. Charlson, J. E. Lovelock, M. O. Andreae, S. J. Warren, Oceanic phytoplankton, atmospheric sulphur, cloud albedo and climate. *Nature* 1987, 326, 655. doi:10.1038/326655A0

- [2] G. E. Shaw, Biocontrolled thermstasis involving the sulfur cycle. *Clim. Change* 1983, 5, 297. doi:10.1007/BF02423524
- [3] P. S. Liss, P. G. Slater, Flux of gases across the air-sea interface. *Nature* 1974, 247, 181. doi:10.1038/247181A0
- [4] M. O. Andreae, The ocean as a source of sulfur compounds, in *The role of air-sea exchange in geochemical cycling* (Ed. P. Buat-Menard) **1986**, p. 331 (Reidel: Dordrecht, Netherlands).
- [5] A. J. Kettle, M. O. Andreae, D. Amouroux, T. W. Andreae, T. S. Bates, H. Berresheim, H. Bingemer, R. Boniforti, et al., A global database of sea surface dimethylsulfide (DMS) measurements and a procedure to predict sea surface DMS as a function of latitude, longitude, and month. *Global Biogeochem. Cy.* **1999**, *13*, 399. doi:10.1029/1999GB900004
- [6] A. R. Ravishankara, Y. Rudich, R. Talukdar, S. B. Barone, Oxidation of atmospheric reduced sulphur compounds: perspective from laboratory studies. *Philos. Trans. Roy. Soc. B* 1997, 352, 171. doi:10.1098/RSTB.1997.0012
- [7] R. Von Glasow, P. J. Crutzen, Model study of multiphase DMS oxidation with a focus on halogens. *Atmos. Chem. Phys.* 2004, 4, 589.
- [8] E. W. Wolff, H. Fischer, F. Fundel, U. Ruth, B. Twarloh, G. C. Littot, R. Mulvaney, R. Röthliscberge, Southern Ocean sea-ice extent, productivity and iron over the past eight glacial cycles. *Nature* 2006, 440, 491. doi:10.1038/NATURE04614
- [9] S. M. Vallina, R. Simó, Strong relationship between DMS and the solar radiation dose over the global ocean. *Science* 2007, *315*, 506. doi:10.1126/SCIENCE.1133680
- [10] S. M. Vallina, R. Simó, S. Gassó, C. de Boyer-Montégut, E. del Río, E. Jurado, J. Dachs, Analysis of a potential "solar radiation dose-dimethylsulfide-cloud condensation nuclei" link from globally mapped seasonal correlations. *Global Biogeochem. Cy.* 2007, 21, GB2004. doi:10.1029/2006GB002787
- [11] N. Meskhidze, A. Nenes, Plankton and cloudiness in the Southern Ocean. Science 2006, 314, 1419. doi:10.1126/SCIENCE.1131779
- [12] R. Cropp, J. Norbury, R. Braddock, Dimethylsulphide, clouds, and phytoplankton: insights from a simple plankton ecosystem feedback model. *Global Biogeochem. Cy.* 2007, 21, GB2024. doi:10.1029/ 2006GB002812
- [13] M. Chin, D. J. Jacob, Anthropogenic and natural contributions to tropospheric sulfate: a global model analysis. J. Geophys. Res. 1996, 101, 18691. doi:10.1029/96JD01222
- [14] T. S. Bates, B. K. Lamb, A. Guenther, J. Dignon, R. E. Stoiber, Sulfur emissions to the atmosphere from natural sources. J. Atmos. Chem. 1992, 14, 315. doi:10.1007/BF00115242
- [15] J. E. Lovelock, L. Kump, Failure of climate regulation in a geophysiological model. *Nature* **1994**, *369*, 732. doi:10.1038/369732A0
- [16] C. Leck, E. K. Bigg, Source and evolution of the marine aerosol a new perspective. *Geophys. Res. Lett.* 2005, 32, L19803. doi:10.1029/2005GL023651
- [17] A. Saiz-Lopez, A. S. Mahajan, R. A. Salmon, S. J.-B. Baguitte, A. E. Jones, H. K. Roscoe, J. M. C. Plane, Boundary layer halogens in coastal Antarctica. *Science* 2007, *317*, 348. doi:10.1126/ SCIENCE.1141408

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