View metadata, citation and similar papers at core.ac.uk
brought to you by CORE
provided by Digital.CSIC

Opinion
CSIRO PUBLISHING
S. M. Vallina and R. Simó, *Environ. Chem.* **2007**, *4*, 384–387. doi:10.1071/EN07055 www.publish.csiro.au/journals/env

Re-visiting the CLAW hypothesis

S. M. Vallina[A,B,C] *and R. Simó*[A]

[A]Institut de Ciencies del Mar de Barcelona (ICM-CSIC), E-08003 Barcelona, Spain.
[B]Present address: School of Environmental Sciences, University of East Anglia (ENV-UEA), Norwich, UK.
[C]Corresponding author. Email: sergio.vallina@uea.ac.uk, sergio.vallina@gmail.com

Environmental context. Over the last twenty years, large and continued research efforts have been invested in deciphering whether oceanic plankton contribute to the regulation of climate by the production and release of cloud-seeding atmospheric sulfur. Our recent research using globally spread observations and satellite-derived data suggest that biogenic sulfur from the oceans represents a major source of cloud-forming aerosols over much of the pristine southern hemisphere oceans. These climate-cooling sulfur emissions respond positively to incoming solar radiation over seasonal cycles, but show a weak response to anthropogenic global warming foreseen for the current century.

A global negative feedback between biogenic dimethylsulfide (DMS) production by the upper-ocean ecosystems and Earth climate has been suggested to occur through the formation of cloud-forming sulfur aerosols in the troposphere and their impact on cloud albedo and the Earth radiative balance.[1] The so-called CLAW hypothesis, although suggestive and not refuted by evidence hitherto, is still highly speculative and some of its main postulates remain unproven. In this essay we seek to contribute to the current knowledge of the oceanic biogenic sulfur cycle and its potential impact on climate by addressing some relevant open questions regarding the CLAW hypothesis.

What is the climatic factor that drives oceanic DMS production? How does it do so?

Charlson et al.[1] proposed that increases in either sea surface temperature (SST) and/or solar irradiance may be responsible for the concomitant increase of DMS concentrations. The analysis of a global DMS database as well as local DMS time series (BATS in the Sargasso Sea and Blanes Blay in the NW Mediterranean) have revealed that the solar radiation dose in the upper mixed layer (or SRD) is the climatic factor that seems to drive DMS dynamics.[2–4] Thus, DMS usually displays a summer maximum in surface waters, even in regions where a phytoplankton biomass proxy like chlorophyll-a (CHL) shows an annual minimum in summer[5–7] (subtropical and low temperate regions), a feature known as the DMS summer-paradox.[8]

The SRD is highly related to the ultraviolet radiation (UVR) dose in the upper mixed layer of the ocean. It has been experimentally observed that UVR can affect two of the major biological players in the oceanic sulfur cycle: (i) heterotrophic bacterioplankton, prokaryotic organisms that can be both a source and a sink for DMS; and (ii) phytoplankton, the primary producers of dimethylsulfoniopropionate (DMSP), the DMS precursor. The question, then, is which organisms and processes are the SRD possibly acting upon to drive DMS dynamics. Most groups of heterotrophic bacteria take up and metabolise DMSP as a major sulfur source and a proportion of it is converted into DMS.[9,10] Some specialised bacteria are capable of degrading DMS.[11,12] UVR is known to cause DNA damage and can inhibit bacterial activity,[13] so it was suggested that summer-time inhibition of bacterial DMS consumption[14] could contribute to the observed DMS accumulation.[8] UVR has also been observed to produce an increase in the amounts of DMSP and DMS per cell volume in phytoplankton, and an intra-cellular DMSP/DMS conversion system has been suggested to play an antioxidant

Sergio M. Vallina (Oviedo, 1976) has a Bachelor degree in Oceanography from the University of Las Palmas de Gran Canaria (2000), an M.Sc. in Biological Oceanography and Marine Environment – Ecosystem Modelling, from the University Pierre et Marie Curie, Paris VI (2002), an M.Sc. in Applied Physics from the Polytechnical University of Catalonia (2003) and a Ph.D. in Oceanography from the Polytechnical University of Catalonia (2006). His Ph.D. thesis, conducted at the Institute of Marine Sciences of Barcelona – CSIC under the supervision of Rafel Simó, was on biogeochemical modelling of upper ocean sulfur dynamics and its impact on cloud forming aerosols. Currently S.M.V. is a post-doctoral scientist at the University of East Anglia, UK.

Rafel Simó (Barcelona, 1965), has a Bachelor degree in Chemistry from the Autonomous University of Barcelona (1988) and a Ph.D. in Environmental Chemistry from the University of Barcelona (1995). He was a post-doctoral scientist at the University of East Anglia, UK (1996). R.S. is currently a scientific researcher at the Institute of Marine Sciences of Barcelona – CSIC. His research is focussed on ocean-atmosphere-climate interactions, with an emphasis on sulfur biogeochemistry, and covers areas from the study of microscopic plankton ecology to global data analyses.

© CSIRO 2007

1448-2517/07/060384

role to cope with high UVR doses (by scavenging the harmful hydroxyl radical, •OH).[15] Based on a mechanistic model of an oceanic pelagic ecosystem that includes both phytoplankton and bacterioplankton, coupled to a biogenic sulfur cycle, we have suggested that bacteria, although being major players in DMS production and consumption, do not seem to play the main role in controlling DMS seasonality. The model was applied in a one-dimensional (1D) physical frame to the Sargasso Sea, a place where the DMS summer-paradox occurs very markedly. From the analysis of several possible scenarios we conclude that phytoplankton direct production and exudation of DMS in response to SRDs (i.e. UVR doses) and may be the major driver of the DMS summer-paradox.[16]

Is oceanic DMS a globally relevant source of cloud condensation nuclei?

Several local field studies have found significant correlations between DMS, its atmospheric oxidation products, sulfates and cloud condensation nuclei (CCN), mostly over remote clean-air oceanic regions.[17–23] These findings, however, lacked the spatial and temporal coverage necessary to resolve whether this DMS–CCN coupling is widespread and, therefore, relevant for global climate processes. Other works suggested that globally, and especially in the northern hemisphere, most of the atmospheric aerosols and CCN do not come from DMS oxidation but from continental sources.[4,24–26] Anthropogenic emissions of sulfur are larger than those from natural sources.[27,28] In addition, the small-size fraction of sea salt (SS) particles released by breaking waves has been proposed to be a dominant source of CCN over clean-air regions far from continents.[29] Finally, organic aerosols of marine biogenic origin are now being seen as a further, potentially large source of CCN.[30,31]

The analyses of satellite and model-derived global data of several oceanic and atmospheric variables suggest that DMS oxidation can indeed be a major source of CCN over oceanic regions far from continental aerosol sources (like the Southern Ocean) especially in summer.[4] Small SS aerosols, although quantitatively important, do not seem to control CCN seasonality over the Southern Ocean, a region where SS production is amongst the highest of the world because of the constant presence of strong winds. Rather, SS aerosols appear to conform to a fairly constant background of CCN.[22] The seasonality of wind speeds and that of the small-mode fraction of aerosols support these conclusions.[6] Over clean-air ocean regions DMS emissions seem then to control CCN seasonality, and its annual contribution to CCN numbers is estimated to be higher than 60%. Over a global scale, however, the estimated current contribution of DMS to annual CCN numbers is rather moderate, of ∼30%.[4] However, because of the strong seasonal coupling of CHL, DMS and CCN over the Southern Ocean,[6] these works[4,6] could not rule out the influence of biogenically driven organic aerosols on CCN.[31] Since we relied on the linear regression between DMS oxidation and CCN numbers obtained for the Southern Ocean to estimate the regional and global contribution of DMS-derived CCN to total CCN numbers, we were implicitly assuming that the contribution of organic aerosols was minor. Therefore, should the organic source of CCN be found to be important over the Southern Ocean, our estimates of the DMS impact on CCN numbers would likely be overestimates.

What is the timescale at which the suggested 'DMS–CCN–cloud albedo' feedback operates and what is its sign? Can DMS alleviate global warming?

In their original paper, Charlson et al.[31] proposed that DMS emissions and their influence on CCN production, cloud albedo and the Earth radiative balance, may be part of a long-term global thermostatic system driven by biological forces. They suggested that the 'DMS–CCN–cloud albedo' feedback could be acting as a natural cooling mechanism that might also counteract anthropogenic global warming. We applied two global DMS diagnostic models, for which the mixing layer depth (MLD) was a key parameter, to global fields of MLD and CHL simulated by a biogeochemistry model embedded into an Ocean General Circulation Model for both global warming conditions (50% increase of present atmospheric CO_2) and non-global warming conditions (control). We obtained global maps of DMS concentrations for these two scenarios.[32] By this means we estimated the response of DMS to global warming. Results were fairly similar for both DMS models: a rather weak increase of DMS concentrations. Globally it was 1.2%, and only in very few places was the increase higher than 5%. According to these results, therefore, although the sign of the feedback appears to be negative, such a low increase in DMS can hardly significantly counteract the effects of global warming since it represents less than a 2% reduction of the estimated positive radiative forcing attributable to CO_2.[33]

Given that experimental evidence points to the SRD and not temperature as the climatic variable that has a large controlling effect on DMS production, the response of oceanic DMS to global temperature warming is expected to be through indirect effects: the associated shoaling of the upper mixed layer would occur with an increase of the SRD, which would cause an increase of surface DMS concentration. Our model simulations suggest that this increase would be small in a ∼50-year scenario of current warming trends.[32] This contrasts with the 1000–2000% increase in DMS concentrations observed every year in the transition from winter to summer, in response to the seasonal variability of solar radiation. We, therefore, suggest that the 'DMS–CCN–cloud albedo' feedback proposed by the CLAW hypothesis should not be viewed as a long-term thermostatic mechanism (at least on the timescale of anthropogenic global warming) but rather as a seasonal process that contributes to the regulation of the amount of solar radiation that reaches the Earth's biosphere. Such a seasonal feedback is not only contributed by the seasonality of DMS emission but also by the seasonality of the main atmospheric DMS oxidant (the OH radical), which also peaks in summer.[4] The coincidence of both seasonalities greatly increases the efficiency of DMS in CCN formation in summer, when an ecosystem protection against the sun is more needed.

This suggestion does not contradict the CLAW hypothesis, but introduces a new point of view with important implications for the mechanistic grounds of the evolution of the feedback. We can speculate that if a biosphere–climate co-evolution occurs through sulfur emission, the selective pressure onto individuals and/or ecosystems that eventually leads to more or less DMS production is to be found in the adaptation to the conditions of their season of optimal growth. Thus, plankton species and communities better adapted to grow in the highly irradiated (and generally low nutrient) waters characteristic of the summer months are higher DMS producers than species and communities adapted to grow in less irradiated, more nutrient rich, mixed waters. These adaptations built on physiological responses to environmental stressors (oxidative stress caused by high UVR and nutrient deficiency in both primary and secondary producers, DNA damage caused by UVR in bacteria, C and S overflow caused by N and P deficiency in primary producers) happen to affect climate in a way that reduces the environmental stressors.[34–36] We do not know if such a complex negative feedback has been operating through the large environmental changes that have occurred over the long history of the Earth, but observational evidence indicates that it does take place every year with the change of the seasons.

References

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

[2] D. A. Toole, D. A. Siegel, Ligth-driven cycling of dimethylsulfide (DMS) in the Sargasso Sea: closing the loop. *Geophys. Res. Lett.* **2004**, *31*, L09308. doi:10.1029/2004GL019581

[3] S. M. Vallina, R. Simó, Strong relationship between DMS and the solar radiation dose over the global Surface Ocean. *Science* **2007**, *315*, 506. doi:10.1126/SCIENCE.1133680

[4] S. M. Vallina, R. Simó, S. Gassó, C. de Boyer-Montegut, E. del Rio, 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

[5] J. W. H. Dacey, F. A. Howse, A. F. Michaels, S. G. Wakeham, Temporal variability of dimethylsulfide and dimethylsulfoniopropionate in the Sargasso Sea. *Deep-Sea Res. Pt. I* **1998**, *45*, 2085. doi:10.1016/S0967-0637(98)00048-X

[6] S. M. Vallina, R. Simó, S. Gassó, What controls CCN seasonality in the southern ocean? A statistical analysis based on satellite-derived chlorophyll and CCN and model-estimated OH radical and rainfall. *Global Biogeochem. Cy.* **2006**, *20*, GB1014. doi:10.1029/2005GB002597

[7] M. Vila-Costa, R. P. Kiene, R. Simó, Seasonal variability of the dynamics of dimethylated sulfur compounds in a NW Mediterranean site. *Limnol. Oceanogr.*, in press.

[8] R. Simó, C. Pedros-Allio, Role of vertical mixing in controlling the oceanic production of dimethyl sulphide. *Nature* **1999**, *402*, 396. doi:10.1038/46516

[9] R. P. Kiene, L. J. Linn, The fate of dissolved dimethylsulfoniopropionate (DMSP) in seawater: tracer studies using 35s-DMSP. *Geochim. Cosmochim. Acta* **2000**, *64*, 2797. doi:10.1016/S0016-7037(00)00399-9

[10] D. C. Yoch, Dimethylsulfoniopropionate: its sources, role in the marine food web, and biological degradation to dimethylsulfide. *Appl. Environ. Microb.* **2002**, *68*, 5804. doi:10.1128/AEM.68.12.5804-5815.2002

[11] M. Vila-Costa, D. A. del Valle, J. M. Gonzalez, D. Slezak, R. P. Kiene, O. Sanchez, R. Simó, Phylogenetic identification and metabolism of marine dimethylsulfide-consuming bacteria. *Environ. Microbiol.* **2006**, *8*, 2189. doi:10.1111/J.1462-2920.2006.01102.X

[12] D. A. del Valle, D. J. Kieber, R. P. Kiene, Depth-dependent fate of biologically-consumed dimethylsulfide in the Sargasso Sea. *Mar. Chem.* **2007**, *103*, 197. doi:10.1016/J.MARCHEM.2006.07.005

[13] G. J. Herndl, G. Muller-Niklas, J. Frick, Major role of ultraviolet-B in controlling bacterioplankton growth in the surface layer of the ocean. *Nature* **1993**, *361*, 717. doi:10.1038/361717A0

[14] D. Slezak, A. Brugger, G. J. Herndl, Impact of solar radiation on the biological removal of dimethylsulfoniopropionate and dimethylsulfide in marine surface waters. *Aquat. Microb. Ecol.* **2001**, *25*, 87. doi:10.3354/AME025087

[15] W. Sunda, D. J. Kleber, R. P. Kiene, S. Huntsman, An antioxidant function for DMSP and DMS in marine algae. *Nature* **2002**, *418*, 317. doi:10.1038/NATURE00851

[16] S. M. Vallina, R. Simó, T. R. Anderson, A. Gabric, R. Cropp, J. M. Pacheco, A dynamic model of oceanic sulfur (DMOS) applied to the Sargasso Sea: simulating the dimethylsulfide (DMS) summer-paradox. *J. Geophys. Res. – Biogeosci.*, in press.

[17] J. M. Prospero, D. L. Savoie, E. S. Saltzman, R. Larsen, Impact of oceanic sources of biogenic sulphur on sulphate aerosol concentrations at Mawson, Antarctica. *Nature* **1991**, *350*, 221. doi:10.1038/350221A0

[18] G. P. Ayers, J. L. Gras, Seasonal relationship between cloud condensation nuclei and aerosol methanesulphonate in marine air. *Nature* **1991**, *353*, 834. doi:10.1038/353834A0

[19] M. O. Andreae, W. Elbert, S. J. de Mora, Biogenic sulfur emissions and aerosols over the tropical south Atlantic: 3. atmospheric dimethylsulfide, aerosols and cloud condensation nuclei. *J. Geophys. Res.* **1995**, *100*(*D6*), 11335. doi:10.1029/94JD02828

[20] G. P. Ayers, J. M. Cainey, R. W. Gillett, J. P. Ivey, Atmospheric sulphur and cloud condensation nuclei in marine air in the southern hemisphere. *Philos. Trans. R. Soc. Lond. B: Biol. Sci.* **1997**, *352*, 203. doi:10.1098/RSTB.1997.0015

[21] A. D. Clarke, D. Davis, V. N. Kapustin, F. Eisele, G. Chen, I. Paluch, D. Lenschow, A. R. Bandy, et al., Particle nucleation in the tropical boundary layer and its couplings to marine sulfur sources. *Science* **1998**, *282*, 89. doi:10.1126/SCIENCE.282.5386.89

[22] M. O. Andreae, W. Elbert, Y. Cai, T. W. Andreae, Non-sea-salt sulfate, methanesulfonate, and nitrate aerosol concentrations and size distributions at Cape Grim, Tasmania. *J. Geophys. Res.* **1999**, *104*(*D1*), 21695. doi:10.1029/1999JD900283

[23] G. P. Ayers, R. W. Gillett, DMS and its oxidation products in the remote marine atmosphere: implications for climate and atmospheric chemistry. *J. Sea Res.* **2000**, *43*, 275. doi:10.1016/S1385-1101(00)00022-8

[24] R. J. Charlson, S. E. Schwartz, J. M. Hales, R. D. Cess, J. A. Coakley Jr, J. E. Hansen, D. J. Hofmann, Climate forcing by anthropogenic aerosols. *Science* **1992**, *255*, 423. doi:10.1126/SCIENCE.255.5043.423

[25] R. B. Husar, J. M. Prospero, L. L. Stowe, Characterization of tropospheric aerosols over the oceans with the NOAA advanced very high resolution radiometer optical thickness operational product. *J. Geophys. Res.* **1997**, *102*(*D14*), 16889. doi:10.1029/96JD04009

[26] M. O. Andreae, T. W. Andreae, D. Meyerdierks, C. Thiel, Marine sulfur cycling and the atmospheric aerosol over the springtime North Atlantic. *Chemosphere* **2003**, *52*, 1321. doi:10.1016/S0045-6535(03)00366-7

[27] S. J. Smith, H. Pitcher, T. M. L. Wigley, Global and regional anthropogenic sulfur dioxide emissions. *Global Planet. Change* **2001**, *29*, 99. doi:10.1016/S0921-8181(00)00057-6

[28] M. Gondwe, M. Krol, W. Gieskes, W. Klaassen, H. de Baar, The contribution of ocean-leaving DMS to the global atmospheric burdens of DMS, MSA, SO_2, and NSS SO_4. *Global Biogeochem. Cy.* **2003**, *17*, 1056. doi:10.1029/2002GB001937

[29] D. M. Murphy, J. R. Anderson, P. K. Quinn, L. M. McInnes, F. J. Brechtel, S. M. Kreidenweis, A. M. Middlebrook, M. Posfai, et al. Influence of sea-salt on aerosol radiative properties in the Southern Ocean marine boundary layer. *Nature* **1998**, *392*, 62. doi:10.1038/32138

[30] C. D. O'Dowd, M. C. Facchini, F. Cavalli, D. Ceburnis, M. Mircea, S. Decesari, S. Fuzzi, Y. J. Yoon, et al., Biogenically driven organic contribution to marine aerosol. *Nature* **2004**, *431*, 676. doi:10.1038/NATURE02959

[31] N. Meskhidze, A. Nenes, Phytoplankton and cloudiness in the Southern Ocean. *Science* **2006**, *314*, 1419. doi:10.1126/SCIENCE.1131779

[32] S. M. Vallina, R. Simó, M. Manizza, Weak response of oceanic dimethylsulfide to upper mixing shoaling induced by global warming. *Proc. Natl. Acad. Sci. USA* **2007**, *104*, 16004. doi:10.1073/PNAS.0700843104

[33] L. Bopp, O. Boucher, O. Aumont, S. Belviso, J. L. Dufresne, M. Pham, P. Monfray, Will marine dimethylsulfide emissions amplify

or alleviate global warming? A model study. *Can. J. Fish. Aquat. Sci.* **2004**, *61*, 826. doi:10.1139/F04-045

[34] R. Simó, Production of atmospheric sulfur by oceanic plankton: biogeochemical, ecological and evolutionary links. *Trends Ecol. Evol.* **2001**, *16*, 287. doi:10.1016/S0169-5347(01)02152-8

[35] R. Simó, From cells to globe: approaching the dynamics of DMS(P) in the ocean at multiple scales. *Can. J. Fish. Aquat. Sci.* **2004**, *61*, 673. doi:10.1139/F04-030

[36] J. Stefels, M. Steinke, S. Turner, G. Malin, S. Belviso, Environmental constraints on the production and removal of the climatically active gas dimethylsulphide (DMS) and implications for ecosystem modelling. *Biogeochemistry* **2007**, *83*, 245. doi:10.1007/S10533-007-9091-5

Manuscript received 30 August 2007, accepted 25 October 2007