

The Effect of Marine Phytoplankton on Global Warming; A Modeling Approach

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ABSTRACT

The possible influence of the marine biogeochemical sulfur cycle on the global climate has been a topic of much recent research. Based on the hypothesis that phytoplankton could affect cloud albedo by producing dimethylsulfide, which is a precursor to aerosols and cloud condensation nuclei, and that cloud albedo could in turn affect the productivity and fitness of the phytoplankton. The presence of such a feedback cycle would have significant implications for models of global climate change. By considering available data on the relationships between individual components of the proposed feedback, a computer aided model was attempted to analyze the cycle as a whole, allowing an assessment to be made of the degree to which the cycle could thermostatically regulate the climate.

INTRODUCTION

In 1983 Shaw, and in 1987 Charlson proposed that a marine biogeochemical sulfur cycle could act as a planetary "thermostat"- a negative feedback loop which would tend to stabilize the climate against perturbations such as warming due to anthropogenic production of carbon dioxide. The mechanism involves the production of dimethylsulfide (DMS) by oceanic phytoplankton and its transport to the marine boundary layer. The DMS particles are then oxidized into methanesulfonic acid (MSA) or sulfur dioxide (possibly even SO_2). These components are then further oxidized to form sulfate particles, which in turn form cloud condensation nuclei (CCN). An increase in the CCN is believed to cause an increase in the amount of droplets that are found in clouds. This increases the amount of radiation that is scattered, hence increasing cloud albedo by way of the "Twomey effect." The Twomey Activation Theory states that activation particles for clouds depend not only on size, but also on solubility. Because of this variation in size and solubility, the cloud activation process is extremely complex and ends up being nonlinear. When the cloud albedo is increased, it decreases the amount of radiation that reaches the surface, which is expected to affect phytoplankton productivity and fitness. Increased aerosol concentrations are also expected to have an effect on *planetary* albedo by reflecting a portion of the radiation back into space. If these conditions exist and cause the phytoplankton productivity to decrease, then a negative feedback loop exists, which might aid in thermostatically regulating the climate.

To analyze the negative feedback loop, it will help to break it down into three components: 1) The connection between phytoplankton and CCN, 2) the effect of changes in CCN levels on cloud albedo, radiation at the surface, and surface temperature, and 3) the response of phytoplankton to the changes in radiation and seawater temperature. Though there is

not yet a consensus on the connection between phytoplankton and CCN, there is a great deal of research that indicates that increased sulfur emissions could have a significant cooling effect on the global climate. The cooling would take place due to direct reflection of radiation by the aerosols and by indirect modification of the cloud albedo. The cooling effect due to sulfur aerosols has been computed to be similar in magnitude to the warming expected from anthropogenic greenhouse gases (Charlson, 1992), thus indicating a plausible feedback system.

MATERIALS AND METHODS

In this project a computer will be used to analyze the feedback cycle as proposed above. The first and third components will be derived by using the chemical, physical, and biological properties of the constituents involved. The second component will be based on an estimate by Charlson, 1987 and 1992, that a 30% increase of CCN in the area covered by marine stratiform clouds would cause a decrease in the global average surface temperature of 1.3 °C, along with the conclusion that enhanced sulfur emissions could cause roughly the same magnitude of cooling by aerosol scattering as by the cloud albedo modification effect. This model will then be used to estimate the strength of the feedback cycle as a whole. This might help us better understand the significance of this oceanic feedback cycle.

RESULTS and DISCUSSION

Connection Between Phytoplankton and CCN

When looking at condensation nuclei in the marine environment, it has been found that they are primarily made up of sulfate aerosols. At this time the best known source for sulfur in the marine environment is DMS, and the best known source for DMS is

phytoplankton. This would indicate that there may be some sort of connection between phytoplankton and CCN.

The Relationship Between Phytoplankton and DMS

The first step in developing a pathway between phytoplankton and CCN is to look at the relationship between phytoplankton and DMS. DMS is believed to be excreted from the phytoplankton when they break down DMSP (dimethylsulfoniumpropionate) and when zooplankton graze on the phytoplankton. When zooplankton graze, they destroy the phytoplankton cells and thereby release the DMS that was inside. The precise pathway that leads to the production of DMS is still not fully understood, and DMS production varies greatly between species of phytoplankton.

Though it is possible to directly measure the population density of phytoplankton, most research in this field attempts to relate phytoplankton to DMS by using indirect data such as chlorophyll *a* and primary productivity. The only direct measurement that was found indicated that there was a strong linear correlation between phytoplankton population and the concentration of DMS found (the correlation coefficient: $r=0.99$ with a level of significance $> 99.5\%$). Several other studies have shown a positive correlation between chlorophyll *a* and DMS through the use of indirect measurements (see Table 1). These studies strongly indicate that there is a connection between marine phytoplankton and DMS.

Table 1. Correlations Found Between Chlorophyll *a* and $[DMS]_{SW}$

<i>r</i>	<i>n</i>	alpha	Reference; Location
0.67	135	<0.005	Barnard [1982]; Atlantic Ocean
0.53	225	<0.001	Andrea & Raemdonck [1983]; Pacific Ocean
0.58	29	<0.001	Cline & Bates [1983]; Equatorial Pacific Ocean
0.57 ^a	166	<0.001	Andreae & Barnard [1984]; Atlantic Ocean
-0.17	51	<0.2	Andreae & Barnard [1984]; Sargasso Sea
0.06	not stated ^b		Leck [1990]; Baltic Sea time series
0.89	14	<0.001	Leck [1990]; Baltic Sea

The correlation coefficient is *r*, *n* is the number of samples, and alpha is the level of significance where $p = 1 - \alpha$ is the probability that $1 - r^2$ of the variation in $[DMS]_{SW}$ can be explained by variations in chlorophyll *a*.

^a Following a log-log transform to make the data normally distributed.

^b Eighteen months of data.

The Relationship Between DMS and CN The next step to consider is the transfer of the DMS from the saltwater into the air to form aerosols. This step must be broken down into two steps in order to deal with the complexity it presents. The first step will be to calculate the DMS flux from the ocean to the marine boundary layer based on the DMS concentration in the ocean.

Calculation of the DMS flux (F_{DMS}) from the DMS concentration in the ocean ($[DMS]_{SW}$) is done through the use of the "stagnant film model" [Liss and Slater, 1974]. This model computes the flux that occurs across the liquid/gas interface based on concentrations of components on each side of the boundary:

$$F_{DMS} = K_v[DMS]_{SW} \quad (\text{Equation 1})$$

The values given for K_v , which is the mean piston value, range from 2.3 m d^{-1} to 4.0 m d^{-1} . It is thought that 2.3 to 2.7 are probably the more accurate measurements. The value of K_v is not a true constant, but depends on meteorological weather conditions. Specifically, K_v increases approximately as the wind velocity squared. This would suggest that global wind patterns, brought on by climatic change, could have a significant effect on regional DMS fluxes. However, it has been shown that the mean piston velocity varies less than 20% between winter and summer. Hence, for long term average calculations, it would seem that the stagnant film model would be an effective way to compute the DMS flux. To perform the calculations I will use the equation above with the K_v value of $2.5 \pm 0.2 \text{ m d}^{-1}$ which is the area-weighted global annual mean [Bates, 1987].

The next step in understanding the relationship between DMS and CN is to look at the connection between F_{DMS} and CN. A strong linear correlation was found by Bates, who compared summer and winter CN data from three southern latitudes with DMS flux (F_{DMS}) data for corresponding seasons in the northern latitudes. A database of CN and F_{DMS} measurements was formed and grouped according to region and season (see Table 2). In the database, K_v varies greatly due to the season and the region where the measurement was taken. Since their model calculated particles based solely on DMS oxidation, a base figure of 80 cm^{-3} was added to the CN column in order to compensate for the non-DMS sources (ie. sea-salt aerosols). The equation used to calculate nonlinear regression for CN in Bates's model is the following:

$$[CN] = A \ln(F_{DMS} + 1) + B \quad (\text{Equation 2})$$

In this equation we can transfer DMS flux (F_{DMS}) from our previous equation to calculate [CN]. A and B are both constants and have the following values: $A = 184 \pm 34$ and $B = 43 \pm 61 \text{ cm}^{-3}$. Though there is still debate on whether to use linear or nonlinear

Table 2 DMS flux and CN Measurements				
Latitude	DMS in SW	Kv	DMS flux	CN
65 - 80 (Arctic), Fall				
65 - 80 N	1.5	1.5	2.3	
68 - 69 S				325
Mean			2.3	325
50 65 (Subarctic), Winter				
53 N			0	80
53 S			0	80
Mean			0	80
50 - 65 (Subarctic), Summer				
55 - 65 N	3.1	1.6	5	
53 N			0.7	140
53 S			0.6	240
Mean			2.1	190
35 - 50 (Temperate), Winter				
38 S	0.3	3.4	1	
41 S				200
41 S				200
45 - 50 N				252
Mean			1	217
35 - 50 (Temperate), Spring				
35 - 50 N	0.8	2.8	2.2	
38 S	0.8	2.8	2.2	
30 - 47 N	2.5	2.8	7	
35 - 50 N	1.6	2.8	4.5	
41 S				300
41 S				300
Mean			4	300
35 - 50 (Temperate), Summer				
35 - 50 N	2.5	2.2	5.5	
38 S	1.5	2.2	3.3	
41 S				375
41 S				450
45 - 50 N				594
Mean			4.4	473
30 -50 (Temperate Fall)				
35 - 50 S	2.8	2.8	7.8	
38 S	0.7	2.8	2	
32 - 40 S	0.8	2.8	2.2	

Latitude	DMS in SW	Kv	DMS flux	CN
35 - 50 N	3	2.8	8.4	
41 S				350
41 S				375
Mean			5.1	363
20 - 35 (Subtropical), Winter				
20 - 35 N	0.7	3	2.1	
30 N			0.5	80
30 S			0.4	80
Mean			1	80
20 - 35 (Subtropical), Summer				
20 - 35 N	2	2.4	4.8	
30 N			1.3	170
30 S			1.3	400
30 - 35 N				230
20 N				180
Mean			2.5	245
5 - 20 (Tropical), Spring				
5 - 20 N	1.8	2.7	4.9	
10 - 30 N	1.2	2.7	3.2	
5 - 20 N	1.8	2.7	4.9	
5 - 20 S	1.5	2.7	4.1	
14 S				325
Mean			4.3	325
5 - 20 (Tropical), Fall				
5 - 20 S	1.1	2.7	3	
10 - 32 S	0.6	2.7	1.6	
5 - 20 N	2.5	2.7	6.8	
14 S				325
Mean			3.8	325
0 - 5 (Equatorial), Annual				
5 S - 5 N	2.8	1.7	4.8	
5 S - 5 N	3.5	1.7	6	
10 S - 10 N	0.9	1.7	1.5	
5 S - 5 N	3	1.7	5.1	
5 S - 5 N	1.5	1.7	2.6	
5 N			1.1	210
5 S			1.2	290
5 N			1	260
5 S			1.3	410
Mean			2.7	293

Table 3. Data for the Relationship Between [CN] and [CCN]

Region	Season	[CN]	[CCN]	S	[CCN]/[CN]	Reference
Cape Grim	winter	122	47	1.0	0.4	Gras [1987, 1989]
Cape Grim	summer	366	176	1.0	0.5	Gras [1987, 1989]
Cape Grim	annual	---	---	0.23	0.25	Ayers & Gras [1991]
Off WA Coast	winter	252	37	1.0	0.15	Hegg [1991]
Off WA Coast	spring	272	52	1.0	0.2	Hegg [1991]
Off WA Coast	summer	594	124	1.0	0.2	Hegg [1991]
Off CA Coast	summer	256	181	1.0	0.7	Hudson & Frisbie [1991]
Off HI	summer	172	115	0.8	0.7	Hudson [1993]

[CN] and [CCN] are particle concentrations per cubic centimeter; S is the supersaturation (in percent) at which the CCN are active.

regression it is clear that there is a strong correlation between DMS flux and CN. Arguments for the use of nonlinear regression models include: 1) the branching ratio of oxidation products of DMS (MSA and SO₂) is very temperature dependant [Hynes, 1986]; 2) the growth of the sulfate aerosols depends on ambient conditions, such as initially present [SO₂] and relative humidity [Lin, 1992]; 3) the atmospheric segment of the DMS cycle may be coupled with other cycles such as sea-salt aerosols [Chameides and Stelson, 1992] and nitrogen [Dentener and Crutzen, 1993]; and 4) particle formation may occur primarily in brief bursts of extreme levels of production resulting in [CN] levels in excess of 3000 cm⁻³, followed by periods of no production during which the newly produced particles are diffused in the boundary layer to give the normal background levels [Covert, 1992; Hegg, 1992]. Because of this evidence the nonlinear regression formula will be used.

The Relationship Between CN and CCN Levels The relationship between CN and CCN is the final step to consider in the pathway between phytoplankton and CCN. Instead of actually modeling particle growth, this study will look at this step in an empirical manner. The growth process from CN to CCN is rather complex and is dependant on many ambient parameters [Lin, 1992]. However, many studies show that over long periods of time there is a linear relationship that tends to emerge. The strength of this correlation was observed to have a linear correlation coefficient of 0.914 between CN and CCN for 30 horizontal flights made in the "below-cloud remote marine boundary layer" [Hudson and Frisbie, 1991]. A survey of the studies, in which simultaneous measurements of CN and CCN were made, is summarized in Table 3 [Ayers, 1991]. In this table there seems to be a conflict in determining an appropriate ratio. Studies conducted by Hudson, 1993 and Hudson and Frisbie, 1991, show that 70% of the measured CN belonged to the subclass CCN. However, in studies conducted by Hegg, 1991 and Ayers and Gras, 1991, there is a

significantly lower percentage of CN found in CCN (20-25%). Gras, in 1987 and 1989, falls between the two extremes (40-50%). It is likely that the discrepancy stems from environmental factors in the regions from which the samples were taken. In this study, a ratio must be adopted, so the assumption will be made that the correct ratio is approximately the average of the ratios found in Table 3. The average of these five studies will be the ratio used in the following equation where CCN and CN are both in cm³ and where A is the value for the averaged ratios which is 0.46 ± 0.24:

$$[\text{CCN}] = A [\text{CN}] \quad (\text{Equation 3})$$

Phytoplankton Response to Radiation and Temperature Change

The next step in the analysis of the proposed feedback loop is to examine the relationship between phytoplankton growth and climatic parameters. Specific attention will be dedicated to: 1) the temperature of the surrounding seawater and 2) the amount of radiation the phytoplankton are exposed to.

The Effects of Radiation of Phytoplankton The relationship between radiation (incident irradiance) and primary productivity (photosynthetic rate) for phytoplankton has been observed by marine biologists. A logarithmic coupling between photosynthetic rate and specific growth has also been established and will be used below [Eppley, 1972; Malone, 1982]. Measurements of photosynthetic rates will almost always increase rapidly in response to increased irradiance. Then at some point, the rates will fall off slowly due to photo-inhibition at higher light intensity. This model describes the major function of the relationship and was developed by Platt, 1980:

$$P_r = P_s (1 - e^{-a_i I_i / P_s}) (e^{-B_i I_i / P_s}) \quad (\text{Equation 4})$$

where P_r is the photosynthetic rate, P_s is the maximum photosynthetic rate in the absence of photo-inhibition, I_i is the incident irradiance (W m⁻²) and a_i and B_i are

parameters which indicate the degree to which the phytoplankton are shade or light adapted. P can vary widely due to variation in species and regions, but is typically in the range of 1-10 mg C [Platt, 1980]. The parameter α normally varies from 0.1 to 1.0 and β varies from .001 to .01. A value for e could not be found.

The Effects of Temperature on Phytoplankton Many studies have been done to determine the dependence of growth rate on temperature for particular species of phytoplankton. In many of the species growth rate increases exponentially until it reaches its T_M (maximum temperature) when it falls rapidly. It has been determined that the maximum temperature varies greatly between species of phytoplankton. Phytoplankton are almost always found several degrees below their T_M . The equation used to show response of growth rate to change in temperature was developed by Eppley and Sloan in 1966. The equation is the following where C_1 and C_2 are constants (per day and per degrees Celcius, respectively) and T is the temperature in degrees Celcius:

$$u = C_1 e^{(C_2 T)} \quad (\text{Equation 5})$$

A value of $0.45 \pm 0.15 \text{ d}^{-1}$ will be adopted for C_1 and $0.07 \pm 0.02 \text{ }^\circ\text{C}$ for C_2 [Eppley, 1972]. A value for e could not be found.

CONCLUSION

In this study an attempt was made to use computer modeling to analyze the feedback strength of the Phytoplankton - DMS - Cloud Albedo - Climate Feedback Cycle. At this time information on this topic and applicable equations are extremely difficult to come by. Due to these complications, results were not achieved that corresponded to the goal of the study. However, the rationalization of the feedback process and ability to tie the various portions of the feedback loop together provide a substantially increased understanding in the workings of these environmental interactions. A strong argument has been presented that shows the connection between phytoplankton and CCN. With more time and more detailed resources the study would have been able to produce a magnitude of feedback that would represent the strength of the feedback loop. If there were a chance to start over and take a new angle for this study the approach would be much narrower. The study would probably consist primarily of finding a plausible link between the components of the feedback loop and finding evidence to substantiate the claims.

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