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**VARIABILITY OF ATMOSPHERIC DIMETHYLSULPHIDE OVER THE SOUTHERN  
INDIAN OCEAN DUE TO CHANGES IN ULTRAVIOLET RADIATION**

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## **Abstract**

Dimethylsulphide (DMS) is a climatically important component of global biogeochemical cycles, through its role in the sulphur cycle. Changes in ultraviolet radiation (UV) exhibit both positive and negative forcings on the dynamics of production and turnover of DMS and its precursor dimethylsulphoniopropionate (DMSP). In this study we investigate the net forcing of UV on atmospheric DMS. The work is based on a 10-year record of observed DMS at Amsterdam Island in the southern Indian Ocean, and satellite based retrievals of surface UV and photosynthetically active radiation (PAR). The results show an inverse relationship between UV radiation and atmospheric DMS associated with extreme changes (defined as the greatest 5%) in daily UV, independent of changes in wind speed, sea surface temperature and PAR.

## Introduction

The main source of cloud condensation nuclei (CCN) in the marine troposphere has been suggested to be sulphate aerosol produced mainly from the oxidation of marine derived dimethylsulphide (DMS) [Andreae and Crutzen, 1997]. The flux of DMS from the ocean to the atmosphere is related to the difference in concentration gradient across the ocean/atmosphere interface as well as wind induced turbulence in the upper ocean [Kettle and Andreae, 2000]. The atmospheric concentration of DMS is very small so the concentration gradient is largely a function of surface seawater DMS concentrations [Kettle and Andreae, 2000]. In seawater DMS comes from its precursor, dimethylsulphoniopropionate (DMSP) after intra-or extracellular cleavage by DMSP lyase enzymes that are found in some phytoplankton and bacteria [Liss et al., 1997; Ledyard & Dacey, 1996]. Evidence exists that marine DMS production is influenced by physical turbulence, osmotic shock, pathogen attack by virus and bacteria, and zooplankton grazing [Malin et al., 1994; Burkill et al., 2002; Nguyen et al., 1988; Belviso et al., 1990]. DMSP is produced by macro- and micro-algae, which in turn are influenced by nutrient supply, light, temperature and salinity. Once in seawater, DMS can be consumed by the biota [Kiene, 1992], be ventilated into the atmosphere [Bates et al., 1987] or be photochemically removed [Brimbecombe and Shooter, 1986]. Thus, the amount of DMS in the atmosphere is a function of a number of interrelated biophysical processes.

In this paper we look at the influence of one factor, ultraviolet radiation (UV), on atmospheric DMS levels at daily timescales, as measured over a 10-year period from 1990, at Amsterdam Island in the southern Indian Ocean [Sciare et al., 2000]. Although measurements

from one location cannot be considered representative of the whole Southern ocean the study casts light on the potential impact of global changes in the climate on DMS production.

UV radiation has a role in a number of the key processes controlling DMS concentrations in seawater. UV can cause (i) DNA damage in phytoplankton and bacteria [Herndl et al., 1993; Lindell et al., 1995; Muller-Niklas et al., 1995] and zooplankton [Damkaer and Dey, 1983; Dey et al., 1988] involved in the production of DMS; (ii) promote the cleavage by algae of the DMS precursor DMSP to DMS [Hefu and Kirst, 1997]; (iii) reduce the biological removal of DMS [Slezak et al., 2001] (iv) enhance the photolysis of DMS to other products both in the ocean and atmosphere [Brimblecombe and Shooter, 1986; Hatton, 2002; Kieber et al., 1996]. Respectively, the expected signs of these UV mediated processes are such that an increase in UV results in (i) an increase in DNA damage of phytoplankton and bacteria and subsequent decrease in DMS and DMSP production (ii) an increase in DMSP to DMS photolysis, increasing DMS production for a constant source of DMSP (iii) a decrease in biological removal of DMS increasing DMS concentrations (iv) and an increase of the photolysis of DMS in the seawater and atmosphere giving a decrease in DMS concentrations. The converse is also likely to be the case. An additional UV influenced process (or set of processes) affecting DMS concentrations in seawater for which the sign of the effect is less clear is the release from the phytoplankton of DMSP into the water, in part controlled by the grazing of zooplankton [Sakka et al., 1997]. Many of the above studies have focused on individual processes involving UV and DMS and used laboratory or shipboard experiments. In this study we attempt for the first time to quantify the net UV effect on DMS concentrations in the atmosphere using real observations.

UV radiation varies on a range of timescales from sub-hourly, due to changes in cloud cover and ozone, to decadal changes, due to stratospheric ozone depletion, and even to centennial and millennial scale and beyond through changes in solar output. The largest variation in UV occurs diurnally, followed by changes at the daily scale as atmospheric conditions change. By focusing the study at a daily timescale we aim to sample events when UV varies considerably but changes in other controls on DMS production, including sea surface temperature and, wind are minimal. Many of the UV mediated processes described above are also influenced by changes in photosynthetically active radiation (PAR) the variability of which is similar to that of UV. However, there are some DMS processes for which the effects of UV and PAR differ in their interactions, most notably DNA damage and repair. While UV is mainly responsible for DNA damage, PAR can enhance DNA damage repair [Gieskes and Buma, 1997] such that UV and PAR may have opposite impacts on DMS concentrations.

## **Data and Method**

Daily atmospheric DMS measurements (at 0800 LT) were made at the Pointe Benedicte sampling station at Amsterdam Island (37°50'S, 77°30'E) in the temperate southern Indian Ocean from 1990-2000. The data were collected by compressing air during 15 minutes into electropolished stainless steel canisters. The air from the canisters was pre-concentrated on a Tenax trap held at -80°C, after which it was thermally desorbed and introduced into the gas chromatograph. DMS was quantified with a flame photometric detector [Nguyen et al., 1990; Sciare et al., 2000]. The same analytical procedure, calibration and time of collection (0800 LT) were maintained throughout the whole sampling period. According to Sciare et al., [2000] the

DMS value at 0800LT is representative of the mean daily DMS concentration (in summer) within +/-15%.

Sea surface temperature (SST) and wind data were obtained from the local meteorological station (referenced as WMO / 61996). Insolation data were also available from this station but were in the form of duration of exposure and were not used in this study. Instead, information on UV and PAR was derived from satellite-based datasets. UV estimates have been derived from observations of ozone amount, cloud transmittance, aerosol amounts, and surface reflectivity from the solar UV radiation backscattered from the Earth's surface and atmosphere as measured by the Total Ozone Mapping Spectrometer (TOMS), and independently measured values of the extraterrestrial solar irradiance [Herman et al., 1999]. These UV data are in the form of Erythemal Exposure data (EUV), an estimate of the integrated daily UV that is likely to cause erythema (sunburn to Caucasian skin), and can be interpreted as an index of the potential for biological damage due to solar irradiation, given the column ozone amount and cloud conditions as determined from TOMS. It should be noted that the units of exposure are arbitrary. Most locations on the Earth are viewed only once per day by the TOMS instrument, so large discrepancies can exist between TOMS-estimated exposures and ground-based measurements. Comparisons of EUV amounts calculated from ground based spectrometers with those from TOMS data show the TOMS based products overestimate EUV by up to 25% for non mountainous and snow and ice free conditions, a result of local fog, clouds smaller than the satellite field of view and undetected UV-absorbing aerosols near the ground [Kalliskota et al., 2000]. These TOMS EUV data are available from the World Wide Web server for the TOMS project at NASA Goddard Space Flight Center at <http://toms.gsfc.nasa.gov/>.



Satellite estimates of PAR data have been derived using the Global Energy and Water Cycle Experiment Short-wave Radiation Budget (SRB) algorithm [Whitlock et al., 1995; Pinker et al., 1995]. The satellite data input to the algorithm is cloud cover obtained from the D1 product of the International Satellite Cloud Climatology Project (ISCCP). Both satellite-based datasets have been validated against surface in-situ observations. The PAR dataset is available from the Department of Meteorology, University of Maryland at <http://www.atmos.umd.edu/~srb/par/01project.htm>).

Unfortunately, the PAR data are only available from 1<sup>st</sup> January 1990 to 5<sup>th</sup> June 1993, the wind speed data from 1st December 1991 to 31<sup>st</sup> December 1999 and the SST data from 1<sup>st</sup> December 1992 to 31<sup>st</sup> December 1999. The EUV record has a missing period of data from 7<sup>th</sup> May 1993 to 24<sup>th</sup> June 1996 due to the orbit of the satellite Meteor-TOMS, which rendered the observations unsuitable for EUV retrievals (Jay Herman personal communication). Thus, due to the limited period for which PAR was available time sequences were selected separately for EUV, DMS and PAR as well as DMS, EUV, wind and temperature. All these data were converted to daily differences by subtracting the value of the previous day.

In this study composite analysis is used to quantify the variability of DMS associated with variability in EUV. This involves selecting a sample of key dates where large changes in daily UV occurred. The daily change in EUV (EUV<sub>d</sub>) is the first difference of EUV defined as

$$\text{EUV}_d = \text{EUV}_{(t)} - \text{EUV}_{(t-1)} \quad (1)$$

where  $EUV(t)$  is the EUV value estimated on day  $t$ . A key date is defined when  $EUV_d$  is greater (or less) than 2 standard deviations (an  $EUV_d$  value of 2000) from the mean  $EUV_d$ , averaged over the entire record. This sample of key dates defines the sampling basis used for composite analysis. The composite mean of DMS (and the other variables, PAR, SST, wind speed) is calculated for the key date and each of the 5 days prior and after. This allows analysis of the mean variation in DMS (and other parameters) associated with extreme changes in EUV. To evaluate this we use a t-test to test the null hypothesis that there is no statistically significant difference in the mean value of each variable on the key date compared with the day prior.

Furthermore, to isolate the potential effect of EUV on DMS from that of other relevant variables (PAR, SST, wind speed) the sample of extreme EUV event key dates (over which the composite mean values of DMS is derived) was restricted (i.e. sub-sampled) to those events where variation in other parameters was minimal. This has the effect of ‘cleaning’ the sample to exclude other competing influences on DMS, such that the influence of EUV is independent of those other factors.

Table 1 gives the dates for the key dates defining the extreme EUV events. All of the events occurred during the summer months of October to March. According to Sciare et al. [2000] DMS in the austral summer has a local origin and thus can be compared to local conditions (including EUV, wind speed and sea surface temperature; see Sciare et al., [2001] for more details). This contrasts with the austral winter when transport can be of the order of several hundred kilometres.

## Results

Figures 1 and 2 depict the sample mean daily values of atmospheric DMS and EUV for extreme increases and decreases, respectively, in EUV. Table 2 shows the mean daily changes (at the key date) in atmospheric DMS, wind speed and sea surface temperature for extreme increases and decreases in EUV. The results show a statistically significant (at the 0.05 level) mean decrease of 40% (133.6pptv) in atmospheric DMS concentration for consecutive days when there was a 66% (2581 EUV) average daily increase in EUV. During these dates there were no statistically significant changes in wind speed. Conversely, for events where EUV decreases by 48% (2738 EUV) DMS increases significantly (at the 0.05 level) by 39% (133, pptv). However, during this sample of events wind speed also shows a significant increase, which could explain the observed change in DMS. By restricting the sample of events used in the composite analysis to only those events where the changes in wind speed were minimal (defined as being between  $\pm 0.5$  standard deviations of the average daily wind speed change) there was an a 29% increase (119.05pptv) in atmospheric DMS for consecutive days when there was an average daily decrease in EUV of 46% (2781 EUV), irrespective of changes in the wind speed.

Sciare et al. [2001] found that wind direction played a role in determining DMS concentrations at Amsterdam Island, with DMS concentrations approximately twice as high during days with northerly winds (between  $280^\circ$  and  $80^\circ$ ) compared with those days with southerly winds (between  $100^\circ$  and  $260^\circ$ ). However, of the chosen dates for extreme changes in EUV we found no systematic change in wind direction before and after the key date. For the extreme increases in EUV events, in 61% of the samples the wind did not change (i.e. remained

from the south or north sectors), in 22% of the samples it changed from the north to the south and in 17% of the samples from the south to the north. For extreme decreases in EUV the wind was from the same direction in 67% of the samples, in 25% of the samples it changed from north to south and in 8% of the samples from south to north.

At a daily timescale photosynthetically active radiation and ultraviolet radiation would be expected to be closely related and indeed a plot of satellite based surface PAR and EUV for the Amsterdam Island grid cell reveals a strong relationship between the two ( $r^2=0.807$ , Figure 3). In an attempt to separate the effects of PAR from UV a sub-sample of key dates of extreme change in EUV were selected during which PAR varied minimally, between  $\pm 0.5$  standard deviations of the average PAR change. Unfortunately, this restricts the analysis to a few events (13 decrease and 6 increase events), but the results indicate that a statistically significant (at the 0.05 level) mean increase of 110% (227.29pptv) in atmospheric DMS, occurs on consecutive days exhibiting a mean decrease of 42% (2415 EUV) in UV, irrespective of changes in PAR (Table 3). It should be noted that the increase in DMS associated with the large decrease in UV, independent of changes in PAR, is considerably larger than that observed when the sample is not divided according to PAR values (Table 2). This might be explained by the counterbalancing impact of PAR on DMS cycle processes such as the promotion of DNA repair. When the threshold used to define an extreme change in UV is reduced (from 2000 to 1000 EUV) and the condition that PAR changes are minimal is maintained there is both a significant (at the 0.05 level), increase and decrease in DMS with decreases and increases, respectively in UV. However, at this threshold the strong relationship between PAR and UV does not allow us to entirely eliminate the role of PAR, which while not showing a significant change at the 0.05

level, still exhibits statistically significant changes at the 0.1 level (i.e. the condition for defining minimal changes in PAR is not stringent enough when the threshold for selecting an extreme UV change is relaxed).

## **Discussion and conclusion**

Atmospheric DMS measurements at Amsterdam Island used in this study can be considered to be representative for an area of about 6° in latitude and 8° in longitude around the island [Sciare et al., 1999]. Seasonally, atmospheric DMS concentrations peak in January during the austral summer and display a minima in July and August during austral winter. Likewise ultraviolet radiation has a similar season cycle (Figure 4). The seasonal cycle of DMS in the atmosphere reflects a similar cycle in DMS concentration in seawater induced by enhanced phytoplanktonic activity [Putaud et al., 1992; Sciare et al., 2000]. At longer interannual timescales there is a variability of up to 50% of the 10-year mean which can only be explained by a change in the ocean DMS concentrations and may be linked to changes in sea surface temperatures [Sciare et al., 2000].

The flux of DMS from the ocean to atmosphere has a thermodynamic constraint (i.e. the chemical potential of DMS across the sea surface, and a kinetic constraint (i.e. wind induced turbulence) [Kettle and Andreae, 2000]. Once in the atmosphere UV further influences DMS through the hydroxyl radical controlled oxidation of the compound. In this study we have focused on extreme changes, both positive and negative, in daily earth surface UV radiation and have quantified the net UV effect on atmospheric DMS concentrations.

Quantifying the role of single parameter (such as UV) in DMS production is problematic using field observations, given such a complex system of biophysical processes, many of which operate simultaneously. To address this we use a methodology based on composite analysis of DMS based on carefully selected samples of daily EUV events in an attempt to isolate the role of UV from that of other controls. Our results indicate that at daily timescales ultraviolet radiation has an inverse relationship with atmospheric DMS concentrations, independent of changes in wind, PAR and sea surface temperature. Whether this can be attributed to processes in the atmosphere or processes in the ocean is not clear and needs further study involving coincident measurements of DMS in seawater, DMS in the atmosphere, its atmospheric oxidation products (DMSO, SO<sub>2</sub>), surface UV, surface PAR, and wind speed over an extended period to sample extremes changes in UV. However, the time of sampling, early in the morning, is likely to render the DMS measurements to be independent of any atmospheric OH oxidation effect observed latter in the day. It is also worth noting that Sciare et al. [2001] found little evidence of any impact of NO<sub>3</sub> or halogen radicals on DMS oxidation [Sciare et al., 2001, Boucher et al., 2002, and J. Sciare, personal communication]. It has also been shown that the positive effect of large decreases in UV on DMS is greater in magnitude when PAR varies minimally than when it does not. While PAR, like UV, varies with cloud cover there are some differences in daily changes in the two variables caused by the different influences of absorption by water vapor and photodissociation by ozone on the two parameters.

Recent work by Sunda et al. [2002] has suggested that DMSP and its breakdown products, including DMS, may serve as an antioxidant system in marine phytoplankton, with species with higher DMSP levels better adapted to the high summertime oxidative stress and explaining why

maximum DMS concentrations in oceanic surface waters occur in the summer when UV exposure is highest. The work described in this study suggests that for short term excessive changes in UV the relationship between the variables can be an inverse one.

One potential implication of this study is that a decrease in stratospheric ozone, and subsequent increase in earth surface UV could cause a decrease in atmospheric DMS. Of course this extrapolation is dependent on the same processes occurring over longer timescales than that considered in this study and with smaller UV changes than the extremes studied here. Finding evidence of any inverse relationship between UV and DMS concentrations at longer timescales is problematic due to the strong positive relationship of PAR with phytoplankton activity and DMS production, and the influence on DMS production of other parameters such as temperature. Further observations are necessary to prove an influence of EUV on DMS at decadal and longer time scales. Finally, it should be noted that these conclusions are based on satellite derived estimates of daily ultraviolet and photosynthetically active radiation with inevitable sampling and retrieval errors.

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**Figure captions**

Figure 1. Composite mean daily EUV and DMS values for a sample of extreme increases in EUV.

Figure 2. Composite mean daily EUV and DMS values for extreme decreases in EUV.

Figure 3. Daily PAR verses daily EUV measurements from 1990-1993.

Figure 4. The average annual cycle of DMS and EUV, at Amsterdam Island, for the years 1990-1999.

## Tables

Table 1. Key dates for extreme increases and decreases in EUV.

| Dates of extreme decreases in EUV |          | Dates of extreme increases in EUV |          |
|-----------------------------------|----------|-----------------------------------|----------|
| 12/07/92                          | 11/13/97 | 12/08/92                          | 02/01/98 |
| 12/13/92                          | 11/21/97 | 12/11/92                          | 02/04/98 |
| 12/15/92                          | 12/15/97 | 12/14/92                          | 11/02/98 |
| 12/18/92                          | 12/20/97 | 12/16/92                          | 12/05/98 |
| 12/23/92                          | 02/07/98 | 12/19/92                          | 01/07/99 |
| 01/01/93                          | 02/12/98 | 12/25/92                          | 01/14/99 |
| 01/12/93                          | 02/18/98 | 12/30/92                          | 01/22/99 |
| 01/19/93                          | 03/30/98 | 01/15/93                          | 01/25/99 |
| 02/08/93                          | 11/08/98 | 01/20/93                          | 01/27/99 |
| 02/12/93                          | 12/04/98 | 11/05/96                          | 02/03/99 |
| 02/27/93                          | 01/04/99 | 11/09/96                          | 02/07/99 |
| 11/08/96                          | 01/21/99 | 11/23/96                          | 10/11/99 |
| 12/19/96                          | 01/24/99 | 12/24/96                          | 10/14/99 |
| 01/06/97                          | 10/03/99 | 12/27/96                          | 10/29/99 |
| 01/20/97                          | 11/06/99 | 01/21/97                          | 12/15/99 |
| 01/25/97                          | 12/04/99 | 11/22/97                          | 12/19/99 |
| 02/18/97                          | 12/14/99 | 12/21/97                          | 12/24/99 |
| 10/29/97                          | 12/17/99 | 12/28/97                          | 12/30/99 |
|                                   |          | 01/25/98                          |          |

Table 2. Mean daily changes in atmospheric DMS, wind speed, sea surface temperature (SST) for extreme EUV events (see text for definition). Statistically significant changes are shown in bold italics.

|  | DMS (pptv)        |                     | Wind speed<br>(ms <sup>-1</sup> ) |                       | SST (°Cx10)   |             |
|--|-------------------|---------------------|-----------------------------------|-----------------------|---------------|-------------|
|  | Day<br>before     | Key<br>date         | Day<br>before                     | Key<br>date           | Day<br>before | Key<br>date |
| <b>Increases in EUV (&gt;=2000).<br/>n=36.</b>                                       | <b><i>506</i></b> | <b><i>301**</i></b> | 6.722                             | 6.194                 | 161.97        | 162.61      |
| <b>Decreases in EUV (&lt;=-2000).<br/>N=37.</b>                                      | <b><i>342</i></b> | <b><i>475**</i></b> | <b><i>5.703</i></b>               | <b><i>7.595**</i></b> | 165           | 164.51      |
| <b>Decreases in EUV (&lt;=-2000)<br/>and minimal change in wind speed.<br/>n=17.</b> | <b><i>405</i></b> | <b><i>524*</i></b>  | 5.778                             | 5.611                 | N/A           | N/A         |

\*\* Indicates statistical significance at 0.05 level

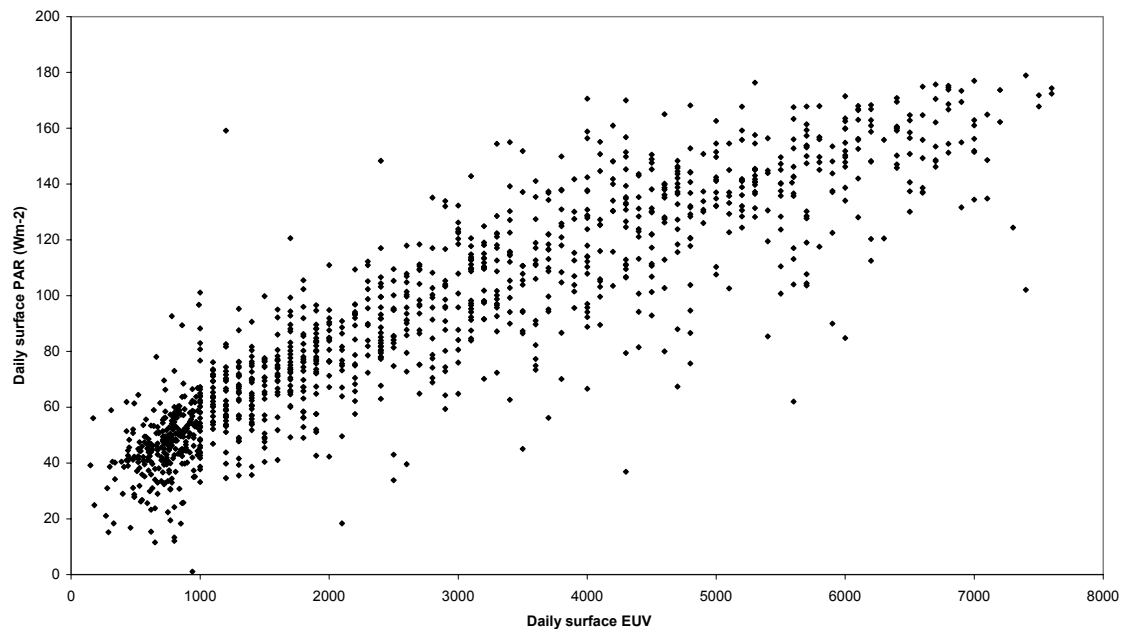
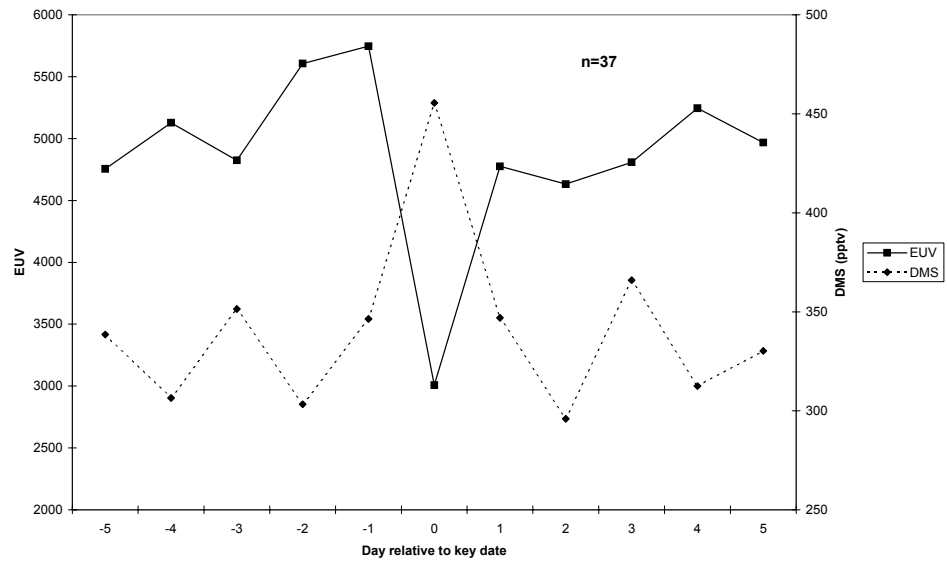
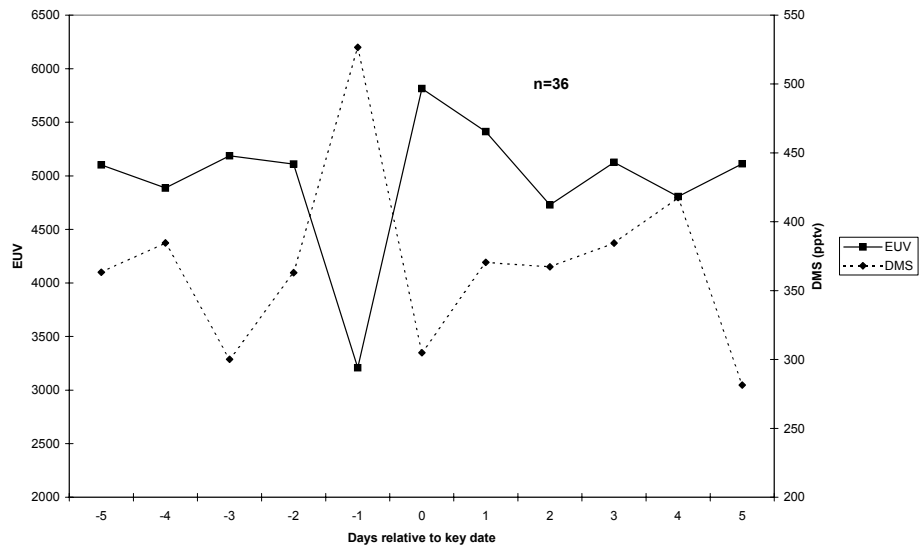
\* Indicates statistical significance at 0.1 level

Table 3. Mean daily changes in atmospheric DMS, PAR and EUV for extreme EUV events (see text for definition). Statistically significant changes are shown in bold italics.

|   | DMS (pptv)        |                     | PAR ( $\text{Wm}^{-2}$ ) |                       | EUV                |                      |
|---|-------------------|---------------------|--------------------------|-----------------------|--------------------|----------------------|
|   | Day<br>before     | Key date            | Day<br>before            | Key<br>date           | Day<br>before      | Key<br>date          |
| <b>Decreases in<br/>EUV (<math>\leq -2000</math>)<br/>and minimal<br/>change in PAR.<br/>n=13</b> | <b><i>206</i></b> | <b><i>434**</i></b> | 129.05                   | 128.72                | <b><i>5730</i></b> | <b><i>3315**</i></b> |
| <b>Decreases in<br/>EUV (<math>\leq -1000</math>)<br/>and minimal<br/>change in PAR.<br/>n=26</b> | <b><i>263</i></b> | <b><i>385*</i></b>  | <b><i>115.86</i></b>     | <b><i>113.98*</i></b> | <b><i>4813</i></b> | <b><i>2918**</i></b> |
| <b>Increases in<br/>EUV (<math>\geq 1000</math>)<br/>and minimal<br/>change in PAR.<br/>n=30</b>  | <b><i>311</i></b> | <b><i>210**</i></b> | <b><i>120.48</i></b>     | <b><i>122.74*</i></b> | <b><i>3250</i></b> | <b><i>4858**</i></b> |

\*\* Indicates statistical significance at 0.05 level

\* Indicates statistical significance at 0.1 level



Figures 1-3.