Determining solar effects in Neptune's atmosphere

Article

Accepted Version

Aplin, K. L. and Harrison, R. G. (2016) Determining solar effects in Neptune's atmosphere. Nature Communications, 7. 11976. ISSN 2041-1723 doi: https://doi.org/10.1038/ncomms11976 Available at http://centaur.reading.ac.uk/64213/

Fathoming solar effects in Neptune's atmosphere

K.L. Aplin, Department of Physics, University of Oxford, Denys Wilkinson Building, Keble Road, Oxford OX1 3RH (karen.aplin@physics.ox.ac.uk)

R.G. Harrison, Department of Meteorology, University of Reading, PO Box 243, Earley Gate, Reading RG6 6BB

Abstract

Long-duration observations of Neptune's brightness in two visible wavelengths provide a disk-averaged estimate of its atmospheric aerosol. Brightness variations were previously associated with the 11-year solar cycle, through solar-modulated mechanisms linked with either ultra-violet (UV) or galactic cosmic ray (GCR) effects on atmospheric particles. Here we use a recently extended brightness dataset (1972-2014), with physically realistic modelling to show that rather than alternatives, UV and GCR are likely to be modulating Neptune's atmosphere in combination. The importance of GCR is further supported by the response of Neptune's atmosphere to an intermittent 1.5 to 1.9 year periodicity, which occurred preferentially in GCR (not UV) during the mid-1980s. This periodicity was detected both at Earth, and in GCR measured by Voyager 2, then near Neptune. A similar coincident variability in Neptune's brightness suggests nucleation onto GCR ions. Both GCR and UV mechanisms may occur more rapidly than the subsequent atmospheric particle transport.

Introduction

Long-term observations of Neptune from a ground-based telescope show small variations in the planet's disk-averaged brightness, which are associated with changes in the reflectivity (albedo) of the planet from its atmospheric aerosol and clouds. Although seasonal variations dominate the time series, Lockwood and Thompson[1] showed, using data from 1972-1996, that small fluctuations in Neptune's brightness at two visible wavelengths followed the 11-year solar cycle. They examined two quantities known to vary closely with solar activity. The first, solar ultraviolet (UV) radiation , is linked to photochemical variations in Neptune's atmospheric aerosol particles, and the second, galactic cosmic rays (GCR) , may create some of Neptune's aerosol through ion-induced nucleation. It was not possible to discriminate between the UV and GCR effects, though the relationship with UV was slightly more statistically robust[1]. The Neptune magnitude-solar activity relationship broke down after 1996[1,2], but recent extension of the data[3] encourages its re-examination. Supporting evidence for a solar cycle in infra-red observations from 1975-2007[4] further motivates a fresh consideration of the origin of the short-term variability in Neptune's albedo.

Both the UV and GCR mechanisms can, in principle, account for the changes observed in the photometric observations, which originate in Neptune's stratosphere and troposphere[1,5]. The UV mechanism was originally proposed[6] to explain the solar cycle signal when it was first reported in Neptune's albedo[7]. It was suggested that UV-triggered surface chemistry on pre-existing aerosol particles varied the optical properties of Neptune's stratospheric aerosol through a darkening in colour ("tanning"), detectable in the photometric measurements. The GCR-driven mechanism was proposed for Neptune[8,9], through direct ("Wilson") condensation of supersaturated gas onto atmospheric ions[10], causing particle growth ultimately detectable at optical wavelengths. The possibility that charge-related effects could modulate the atmospheres of the outer planets, where variations in solar irradiance are proportionately less important[11], contrasts with the likely role of energetic particles in Earth's atmosphere[12], and provides a further motivation for this study.

The two proposed mechanisms for external solar forcing of Neptune are essentially heliospheric (through GCR) or photospheric (through solar UV) in origin. The analysis to investigate them here uses two approaches. Firstly, the relationships between Neptune's magnitude, solar UV radiation and GCRs are studied with multiple regression, allowing both the proposed mechanisms to act together. We find that, when the extra degrees of freedom are accounted for, including both UV and GCR improves prediction of the magnitude fluctuations. Secondly, we examine the relatively rapid fluctuations apparent during the mid-1980s in the Neptune astronomical data. This enhanced variability coincided with a known episode of quasi-periodic variability present in GCR[13], centred around 1.68 years. Investigating Neptune's atmospheric variability in the 1.5 to 2 year range therefore presents a method by which to separate the two different suggested solar-modulated influences, an approach previously employed to separate coincident terrestrial atmospheric responses[14].

Results

The extended Neptune photometric dataset 1972-2014

Regular photometric observations of the magnitude of Neptune have been made since 1972, through well-characterised visible bandpass filters of width ~20nm centred at 472nm ("b", blue) and 551nm ("y", green) using a 21-inch telescope at Lowell Observatory, Arizona[2], fig 1a. Each brightness value is typically determined from between 4 and 39 nights of data (median 9 nights), taken around the time the planet is brightest in the sky (opposition)[3]. Standard errors in the magnitude measurements, determined from the standard deviations and number of nights of observation were typically± 0.001 [3]. Sampling intervals varied between 0.7 and 1.2 years, with median interval of 1.04 years. Fig 1 summarises the data, with Fig 1a showing the measured magnitudes, Fig 1b the magnitude fluctuations, Fig 1c the UV data and Fig 1d GCR measured both at Earth and in space. More information on the data is given in the Methods section.

The correlation between the 29 data points and 30-day running means of UV, sunspots and GCR with a range of lags was calculated previously[1]. The correlation between Neptune's magnitude fluctuations and UV was statistically significant, whereas the correlation with GCR was not, on which basis it was concluded that UV was the more likely mechanism[1]. This analysis[1] did not allow for the possibility that both the physically plausible mechanisms involving UV and GCR could be acting in combination in Neptune's atmosphere to cause the observed albedo variations. If so, multiple regression may be more appropriate than treating the two proposed mechanisms separately. LT02's analysis was statistically rather than physically based, whereas we have used standard ion-aerosol theory to guide our statistical approach. Finally, extra data have recently been made available[3], which we now include.

LT02's analysis assumed a linear relationship between both UV and albedo, and GCR and albedo. Although the UV-albedo relationship is generally assumed to be linear[6], this assumption is not necessarily appropriate for the GCR mechanism. In this case, the albedo changes are likely to be proportional to the number of ion-induced particles. The number of particles formed is controlled by the ion-induced nucleation rate[9], which is proportional to the atmospheric ion (or electron) concentration n, where the ions are singly-charged, nanometre-sized clusters created by GCR ionisation[11] with volumetric production rate q. In ion-aerosol theory, there are two possible limiting regimes linking n and q, firstly, the recombination limit of negligible aerosol, in which the ion concentration n is controlled by ion-ion or ion-electron self-recombination and $n \propto \sqrt{q}$. Secondly, in the attachment regime, the ion concentration is limited by attachment to any pre-existing particles (such as aerosols, haze, clouds or dust) and $n \propto q$ (e.g. [11]). Assuming that the GCR count rate provides an estimate of q (e.g. [15]), a set of possible statistical relationships was investigated of the form:

$$f_{b,y} = \kappa_{b,y} UV + \lambda_{b,y} GCR + \mu_{b,y} \sqrt{GCR} + x_{b,y} \qquad (1)$$

where $f_{b,y}$ are the measured magnitude fluctuations in the b (472nm) or y (551nm) wavelength ranges, κ, λ and μ are coefficients for the b or y data representing the UV mechanism, ion attachment and ion recombination respectively and x is a constant for the b or y data. Daily Lyman-alpha and Oulu neutron counter data, averaged for ± 20 days around the observation date given in [3], were used as measurements of UV and GCR (see Methods section). The regressions were weighted according to the standard errors in the magnitude data described above, and the errors in UV and GCR data were assumed to be negligible in comparison with those in the magnitude data. As the attachment and recombination regimes cannot act simultaneously at the same location, this set of statistical relationships represents the integrated effect of the different atmospheric layers observed at Earth through each filter.

The adjusted coefficient of determination (R^2), i.e. fraction of the variance explained by the fit, corrected for the number of points and fitted variables, was used to evaluate each model, summarised in Table 1. For the *y* filter, adjusted R^2 was improved to 14% (see case 7 in Table 1) when both the UV and GCR-related mechanisms were included rather than considering the mechanisms separately, which only explained 2-8% of the variance. Considering both GCR-created ionisation and UV therefore permits rejection of the null hypothesis, which is that including both UV and GCR does not improve the fit (e.g. [16]). The improvement from including both GCR and UV is less marked for the *b* filter data, with the fit between UV and magnitude fluctuation slightly better than for GCR, UV and magnitude fluctuation. The measured and modelled magnitude fluctuations are compared in figure 2.

One possible explanation for the differences between the *b* and *y* filter responses relates to the different parts of Neptune's atmosphere accessed by each filter. The 442 nm *b* filter responds to stratospheric haze particles, whereas the 551nm *y* filter is more sensitive to the optical properties of tropospheric aerosols[6]. UV will be absorbed by, for example, haze layers[17] as it passes through the atmosphere, whereas highly energetic secondary GCR, typically muons of several GeV, can readily penetrate the deep atmosphere (e.g. [11]), with the maximum ionisation, known in the terrestrial atmosphere as the Pfotzer-Regener maximum[15], expected at about 40 hPa [9]. It is therefore plausible that particles seen by the *b* filter in the haze layers would respond preferentially to UV, but that the changes in the *y* filter wavelength can be better explained by the inclusion of GCR in the model.

Spectral analysis

Particle detectors on the Voyager 2 spacecraft measured primary GCR as they passed out of the Solar System. These measurements showed variability on 1 to 2 year timescales[18], which was at its strongest in primary GCR in the 1980s, consistently with terrestrial neutron monitor data[19]. Although similar variability is apparent in terrestrial GCR (neutron monitor) measurements, it is not in the solar 10.7cm flux, a widely-used index of solar radiative emissions[20]. Beyond GCR data, this variability in the 1980s has also been identified in other heliospherically-modulated quantities[19], such as terrestrial surface atmospheric electricity data[21]. In contrast, such variability is not apparent in photospheric quantities such as solar UV, which makes this periodicity a useful diagnostic for separating photospheric and heliospherically-modulated effects[14].

To pursue this for Neptune's atmosphere we consider whether the cosmic ray variability observed at Earth is also present at Neptune. Having established that it is, we then consider when the variability on these timescales occurs in Neptune's atmosphere, GCR and, for completeness, solar UV. One approach to evaluating variations such as these within specified frequency ranges is to use a periodogram, or a series of periodograms selecting successive time intervals. Using successive periodograms, calculated using the Lomb-Scargle method for irregularly-spaced data, the temporal variations of spectral power density between 1.5 and 1.9 years in Neptune's magnitude, cosmic rays from both Voyager 2 and Oulu and UV (Lyman-alpha) radiation are shown in Figure 3 as a moving window spectrogram. The cosmic ray data used are protons >70 MeV measured by the Voyager 2 Low Energy Charged Particle (LECP) instrument[22]. Figure 3a presents a spectrogram of the data from Voyager 2, indicating the strong spectral power at 1.5-1.9 year periodicities from about 1983-1987, when Voyager 2 was travelling from Saturn to Neptune. (Further details of the spectral data processing are given in the

Methods section). Voyager 2's closest approach to Uranus was on 24/1/86, and to Neptune on 25/8/89 [23].

Figs 3a,b,c show spectrograms generated from data at Neptune, Fig 3d terrestrial cosmic rays measured at Oulu in Finland, and Fig3e the UV data. The Oulu and Voyager 2 cosmic ray data support earlier findings[17], in that the spectral variability appears first in GCR at Earth (fig 3d), before reaching Voyager 2 (fig 3a) consistent with outward propagation of a heliospheric feature. The Neptune and Voyager 2 spectrograms show similarities in their time evolution, with coincident increased spectral power density during the 1980s. To evaluate the significance of this enhanced spectral power density, a Monte-Carlo procedure was used. Many (10000) realisations of the power spectra were calculated using random shuffling of the magnitude fluctuation data, and a peak at ~1.6 years has a probability of being caused by chance of about 1% ($p<0.02$), see figure 4.

In contrast, the spectrogram derived from the Lyman-alpha data (figure 3e) shows minimal variability in the range of periodicities considered during the mid-1980s. Hence the Voyager 2 cosmic ray data establish that the 1.5-1.9 year periodicity was present both in Neptune's atmosphere and in GCR near Neptune during the 1980s.

The 1.5-1.9 year spectral feature in heliospheric GCR can be used as a "fingerprint" of a possible GCR influence in atmospheric properties such as clouds[14]. Comparing the strength of this feature on Neptune with GCR therefore provides a method to separate UV and GCR effects on Neptune's albedo. However, there may be a lag in Neptune's measured albedo in response to external forcing, due to the internal timescales of particle production and movement in Neptune's atmosphere. These processes were described[6] as methane being injected into the stratosphere and upper troposphere by convection, where photochemical, nucleation and sedimentation processes act on timescales of typically a few Earth years. The photochemical colour changes postulated to be the UV mechanism providing solar modulation of the albedo are thought to act on 0.2-2 year timescales[6]. Guided by these ideas, it was found that the fit statistics summarised in Table 1 could be improved by allowing Neptune's albedo to lag UV and GCR.

We have further investigated the delays in Neptune's atmospheric response by carrying out a lag correlation analysis between the average 1.5-1.9 year spectral power density (SPD) in GCR, as for figure 3, and the same quantity in Neptune's magnitude, figure 5a. The peak response is achieved at a lag of 3 years for both wavelengths, and figure 5b indicates that, with a 3-year lag, 32% of the variance in the Neptune 472nm SPD can be explained by GCR at $p<0.001$ confidence (18% for the 551nm SPD at $p<0.05$ confidence). The calculated lag is robust to errors in the SPD, as determined by recalculating the spectra many (10000) times, including a normally distributed random error within the quoted uncertainty on the magnitude measurements[3]. For comparison, fig 6 is a version of fig 5 calculated for the 1.5-1.9 year spectral power density in Lyman alpha (UV) radiation. As the maximum correlation in figure 6a occurred at a 4 year lag, this lag has been used in figure 6b rather than the 3 year lag in fig 5. This difference in lag is unlikely to be important because a 1.5-1.9 year periodicity calculated from the quasi-annually sampled Neptune data gives the lag determination at best 2 year resolution. Unlike the GCR-magnitude relationship in SPD (fig 5) which shows an almost linear dependency in the 1980s, there is no statistically significant linear effect in the data in fig 6 (or, indeed, for the 551 nm SPD against the UV SPD, not shown). This indicates that some of the spectral features previously identified in the GCR data during the 1980s have propagated into Neptune's atmosphere for detection at 472 nm, which is not replicated for the UV data.

Returning to the GCR effects, and restricting the analysis to data from the 1980s, when the spectral feature was particularly strong and known to be present close to Neptune, then 87% of the variance in this intermittent periodicity at 472nm can be explained solely by GCR at the $p<0.001$ confidence level. For the *y* data at 551nm, the R^2 remains 18% during the 1980s.

Estimates using classical cloud physics theory[24] for plausible parameters of ion-induced particle growth at Neptune (see the Methods section) indicate that newly nucleated particles could grow to optical wavelengths relatively quickly, with timescales from tens of minutes to hours. This rapid ion growth timescale implies that the lagged GCR effects observed in Neptune's magnitude fluctuations could arise from the propagation of the 1.5-1.9 year periodicity outwards through the heliosphere, suggested by the lag between the spectral features in Voyager 2 (figure 3a) and Oulu (figure 3d).

The two analyses presented in this paper, multiple regression and spectral analysis, represent different effects. The multiple regression evaluates the net response of Neptune's magnitude to both GCR and UV forcing, whereas the spectral power density approach only addresses the sensitivity of Neptune's atmosphere to one forcing, that of GCR on 1.5-1.9 year timescales. At 472nm, variability at these periodicities during the 1980s is well explained by GCR. In terms of net response over the whole dataset (1972-2014), fluctuations in the 472nm filter data are most effectively accounted for by UV variations alone, but at 551nm there is a combined effect of GCR and UV.

Discussion

Two alternative origins have previously been proposed[2] for the decadal variations observed in Neptune's atmosphere, external forcing (solar modulation), or chance. On the basis of a statistical argument, GCR or UV presented alternatives as solar forcing agents[1]. Including the most recent data, we now find that considering GCR and UV as joint contributors to Neptune's atmospheric variability is stronger than an either-or scenario. Our model's explanatory power is enhanced by including realistic ion-aerosol physics, allowing for ion loss both by attachment to aerosol and by ion-ion or ion-electron recombination.

Ion-aerosol theory considerations indicate that, in cloudy or hazy conditions, ions attach to aerosol particles (see eq 1). This has two consequences. Firstly, haze particles or cloud droplets will become charged by ion attachment. The charge does not depend on the ionisation rate[25], so will not generate the photometric variability analysed here. Secondly, the associated ion depletion will reduce opportunities for ion-induced nucleation. As Neptune's stratosphere and troposphere are rich in haze and cloud particles[5,6], this suggests a role for transport processes[6],[26] in moving nucleated particles to regions where they become detectable in the photometric observations.

Our work provides new evidence for solar forcing in Neptune's atmosphere on sub-seasonal timescales, through both UV-driven and GCR mechanisms. The lags in

Neptune's response to external forcing present in both GCR and UV data over the entire time series, and in the GCR SPD during the 1980s, are consistent both with each other and with known particle movement timescales[6]. Further investigation is needed to understand the potentially very different timescales associated with both particle-modulating mechanisms, and the relevant transport processes within Neptune's atmosphere.

Methods

Neptune magnitude data

The Neptune magnitude data has been collected by Dr W Lockwood and collaborators from Lowell Observatory, Arizona over many years[2,3]. Neptune's magnitude is measured with a 21-inch reflector telescope using differential photometry, a technique based on measuring the brightness of a target object relative to comparison stars. The data is filtered in the visible with filters called "b" (centred on 472nm) and "y" (centred on 551nm). Filter response functions and details of the long term stability and errors are all given in [2].

Detrending the Neptune magnitude data is necessary to remove the slow seasonal-related increase in Neptune's brightness (see e.g. [1,2] and [27]). Following the approach in [1] we have applied smoothing curves to the magnitude data to remove the low-frequency seasonal changes and look at fluctuations occurring on more rapid timescales. A quadratic detrend was applied in earlier analyses[1,2] but rather than assume an arbitrary polynomial, we have applied robust local smoothing methods and compared them to the quadratic in Fig 7a. The lowess28 fit and the newer algorithm, loess29, are well-established non-parametric local smoothers, weighted towards points near the region to be fitted. It can be seen from Fig 7b that the key features in the magnitude fluctuations are preserved independently of the choice of smoothing fit.

A Kolmogorov Smirnov (KS) statistical test has also been used to establish whether the magnitude fluctuations calculated using the different smoothing fits are statistically "different" from each other. Importantly, the KS test does not make any assumptions about the form or distribution of the data (e.g. [30]). Table 2 indicates that for most of the types of smoothing used, the calculated magnitude fluctuations are not significantly different.

Cosmic ray data

Galactic cosmic rays (GCR) are energetic particles generated outside the Solar System. They are mainly protons, which are most abundant, and alpha particles (helium nuclei)[31]. Cosmic rays ionise atmospheres by colliding with molecules and inducing a cascade of secondary ionising and non-ionising particles; they are the major source of ionisation in many planetary atmospheres[11]. Neutron monitor measurements of GCR are used here as an indicator of atmospheric ionisation. Neutrons are non-ionising radiation formed by GCR decaying in Earth's atmosphere and are measured by a network of terrestrial monitors, described below. GCR can also be measured directly by spacecraft. Voyager 2 proton data, available from 1977, is useful for comparison since it represents the cosmic ray flux near or at Neptune for some of the time period of interest. However, because of the variable lag of up to 4 months between the time series of neutron monitor data and Voyager 2 data, depending on the position of Voyager 2, we have chosen to focus on data from the Oulu neutron monitor, which has been in continuous operation since the 1960s[32].

Oulu neutron data

The Oulu neutron monitor detects neutrons generated by primary GCR decaying in the atmosphere. Integrated over the atmospheric column, neutron monitor data is a reasonable proxy for cosmic ray ionisation in Earth's atmosphere (although not necessarily in the lower troposphere[15]). As the physics of atmospheric ionisation is fundamentally similar between Neptune and Earth[11], we use the Oulu data as a source of long-term cosmic ray data. The Oulu neutron monitor is essentially unchanged since installation in the 1960s, but there is an "efficiency" factor applied to the data to include the effects of changes in hardware and software (as well as the routinely applied atmospheric pressure correction). The data are fully explained at http://cosmicrays.oulu.fi/ and in [32]. Our analysis uses one-day averages, although 5-minute resolution data is available from 1968.

Voyager cosmic ray data

The Voyager 2 >70 MeV proton data was obtained by the Low Energy Charged Particle (LECP) instrument[22], although time series of >70MeV ions and high energy alphas and protons from the Cosmic Ray Subsystem (CRS) instrument[33] are similar and could equally have been used. Data (available and described in detail at http://sd-www.jhuapl.edu/VOYAGER/) are sampled at 1s intervals but recorded as daily average count rates, with the standard deviations reported. The median standard deviation was 0.003 s^{-1} (with an interquartile range of 0.002-0.004 s^{-1}) compared to a median count rate of 0.072 s^{-1} i.e. a fractional standard deviation of ± 4%.

Lyman alpha UV data

The Lyman alpha data is a composite time series of the solar hydrogen 121.57 nm emission line, and represents UV emissions from the entire solar disc[34]. It is generated from a combination of satellite measurements and models extending back to 1947, available from http://lasp.colorado.edu/lisird/lya/. For the time period relevant to this paper, the data is taken from the Atmospheric Explorer-E (1977-1980), Solar Mesospheric Explorer SME (1981-1989), the Upper Atmosphere Research Satellite

(UARS) SOLSTICE instrument (1991-2000), Solar Radiation and Climate Experiment (SORCE) SOLSTICE instrument (2003-2010) and Solar Dynamics Observatory (SDO) EVE (2010-2015). The times where no satellite data is available (1972-1977 and 2001-2003) are filled in by model calculations[35]. Detailed discussion of this data set is outside the scope of this paper[35], but the uncertainty is estimated to be ± 10%.

Spectral analysis

The periodograms in Figure 3 were all generated from data selected using a moving window of width 8 years having a 0.5 cosine bell taper, with steps of 0.5 years between successive data window evaluations. The data were first de-trended using a loess fit. (We demonstrated that the fluctuations are insensitive to the choice of detrend used in *Neptune magnitude data* above). The selected data window was cosine tapered (tapering factor 0.5), to reduce the truncation effects of the short data windows. The Lomb-Scargle[36,37] approach for irregularly spaced data was used, with the code[38] implemented in R. In the case of irregularly spaced data, the minimum detectable frequency is $0.5/s$ where s is the minimum sampling period of the dataset. In the Neptune data the minimum sampling interval is 0.7 years, giving a minimum detectable periodicity of 1.4 years[39,40].

The 1.5-1.9 year periodicity described in the GCR data in the Results section was independently confirmed to occur in the 1980s by an additional analysis of the daily GCR data. This analysis used a phase-preserving 1.55-1.81 year Lanczos bandpass filter[41] of half-length 8 years, with missing values replaced by multiple bootstrapped realisations[14]. Computer code is available on request.

Droplet formation from ions in Neptune's atmosphere

Droplet nucleation onto ions

The saturation ratio required for ions to grow into ultrafine droplets by condensation can be determined using the Thomson equation (2), which describes the equilibrium saturation ratio needed for ion-induced nucleation to become energetically favourable[11]. In equation 2 r is radius, ρ fluid density, M the mass of the molecule, q charge, γ_T the surface tension, k_B Boltzmann's constant, T temperature, r_o the initial radius (all in SI units), and ε_r relative permittivity:

$$\ln S = \frac{M}{k_B T \rho}\left[\frac{2\gamma_T}{r} - \frac{q^2}{32\pi^2\varepsilon_0 r^4}\left(1-\frac{1}{\varepsilon_r}\right)\right] \qquad (2)$$

A similar approach was previously taken to calculate the supersaturations at which ion-induced nucleation could occur on Neptune[9]. Here we apply the Thomson equation for methane and diacetylene (butadiyne), two species thought likely to form droplets through ion-induced nucleation at the pressures and temperatures appropriate for Neptune[9]. Diacetylene nucleates onto singly charged ions of critical radius 1 nm at a saturation ratio of 2.33, whereas methane needs a saturation ratio of 8.25 for nucleation onto ions to become energetically favourable (Fig 8). As these saturation ratios are expected in the cold Neptune environment[9], condensation can occur onto freshly produced ~1 nm cluster ions, with no need for additional ion growth or charging. Figure S4 also shows that ion-induced nucleation occurs more easily at lower critical saturation ratios on multiply-charged large ions, consistent with the "relatively efficient" ion-induced nucleation predicted in [[9]].

Droplet growth by condensation

We now estimate the rate of droplet growth for methane condensation at 75K and 1100 hPa on Neptune with methane saturation ratio of 2.7 in a hydrogen atmosphere[9] (There is not enough data available to carry out the calculation for diacetylene).

Following [24], the rate of growth of a droplet of radius r is given by

$$r\frac{dr}{dt} = \frac{S-1}{\left[\left(\frac{L}{R_vT}-1\right)\frac{L\rho_L}{KTf(\propto)}+\frac{\rho_L R_v T}{De_s(T)g(\beta)}\right]} \tag{3}$$

where S is the saturation ratio, T is the temperature, L is the latent heat of vaporisation, R_v is the gas constant for the condensing species, D is the diffusion coefficient for the condensing species, K is the thermal conductivity, ρ_v is the vapour density and $e_s(T)$ is the saturation vapour pressure. Two normalisation factors, $f(\alpha)$ and $g(\beta)$, are also defined[24] where

$$f(\propto) = \frac{r}{r+\left(\frac{K}{\propto p}\right)\frac{\sqrt{2\pi R'T}}{c_v+R'/2}} \tag{4}$$

with p the pressure and R' the gas constant of the background gas, and α is 1. The second normalisation factor is given by

$$g(\beta) = \frac{r}{r+\frac{D}{\beta}\sqrt{\frac{2\pi}{R_vT}}} \tag{5}$$

where $0.02 < \beta < 0.04$ and is taken here to be 0.04. The terms used in the calculation are listed in Table 3.

Inserting values from Table 3, we find that the estimated droplet growth rate is of order 4 nm s^{-1}, which is insensitive to both the initial radius, and the radius as the droplet grows. This insensitivity to radius arises from the $1/r$ term in eq 3 being essentially cancelled out by the r terms in eqs 4 and 5.

Author contributions and acknowledgements

KLA carried out the statistical analysis and RGH the spectral analysis. Both authors contributed equally to other analysis and manuscript preparation. There are no conflicts of interest. We acknowledge the commitment and dedication of Dr W Lockwood in maintaining the Neptune observations for over forty years.

Figure legends

Figure 1 Time series of Neptune's brightness, solar ultra-violet radiation and galactic cosmic rays. (a) Neptune brightness (astronomical magnitude, where smaller values represent a greater signal) time series at 472nm (blue squares) and 551nm (green circles), from [3], each smoothed with a lowess fit (blue dashed line or green solid line). (b) Magnitude fluctuations after detrending (a) with a lowess fit. The maximum standard error on the mean in each dataset is shown as a single error bar on the far left. (c) Lyman alpha (ultra-violet) radiation at 121.5nm (10^{11} photons cm^{-2} s^{-1}). (d) Cosmic ray count rate at Earth's surface and in the heliosphere, showing terrestrial neutron monitor data from Oulu, Finland, in daily averaged counts min^{-1} (black) and Voyager 2 Low Energy Charged Particle (LECP) instrument daily mean flux of cosmic ray protons > 70MeV (grey) in min^{-1} (standard deviations are typically 4%). Data are described in full in the Methods section.

Figure 2 Physically realistic linear regression models to explain Neptune magnitude fluctuations. The models include ultra-violet radiation, attachment and recombination of galactic cosmic ray-created ions - Case 7 in Table 1 - for (a) f_y at 551 nm and (b) f_b at 472 nm. The coefficients determined in equation (1) for, respectively, (a) κ=0.010±0.004 cm^2s, λ=(2±1)x10^{-4} min, μ=-0.04±0.02 $min^{0.5}$, x=1.5±0.8 mag (where mag is astronomical magnitude), and (b) κ=0.011±0.005 cm^2s, λ=(2±1.5)x10^{-4} min, μ=-0.03±0.02 $min^{0.5}$ and x = 1.1±0.9 mag.

Figure 3 Spectral power densities between 1.5 and 1.9 years for Neptune, ultra-violet and galactic cosmic rays. Moving window spectrograms derive the spectral power density, normalised by the variance to be dimensionless, for periodicities between 1.5 and 1.9 years from (a) the Voyager 2 Low Energy Charged Particle (LECP) instrument proton data, (b) Neptune's magnitude fluctuations at 551nm, (c) 472nm, (d) Oulu neutron monitor data, and (e) solar ultra-violet (Lyman alpha) radiation. Contours of spectral power density are shown, with colour for added emphasis. The data and spectrogram calculations are described in full in the Methods section.

Figure 4 Estimate of statistical significance of the spectral power density (SPD) at 1.5-1.9 years during the 1980s. Power spectra (solid lines) calculated for the 472 nm and 551 nm magnitude data 1980-1994, using the Lomb-Scargle method after de-trending using a loess fit. The statistical significance of the spectral peaks has been evaluated using a Monte-Carlo procedure: dashed and dotted lines show the upper 95th and 99th percentiles of 10000 realisations of the power spectra calculated in the same way, but after random shuffling of the magnitude data.

Figure 5 **Relationships between 1.5-1.9 year spectral power densities for Neptune and galactic cosmic rays** (a) Correlation between mean normalised spectral power density (SPD) for periodicities between 1.5 and 1.9 years in Neptune's atmosphere against the same periodicity in galactic cosmic rays (GCR) at Oulu, for Neptune lagging Oulu by 0-10 years. Dotted lines mark 95% confidence limits from multiple (10000) realisations of the SPDs calculated with the uncertainties in the magnitude fluctuations. (b) Average Neptune 472nm SPD against GCR SPD data values for the 1.5-1.9 year periodicity, with Neptune lagging Oulu by 3 years. The filled circles are from 1980-1989, when the 1.5-1.9 year periodicity was particularly strong, and the rest of the data are open circles. A lowess fit to all the data points is also shown (solid line).

Figure 6 Relationships between 1.5-1.9 year spectral power densities for Neptune and ultra-violet radiation Correlation between mean normalised spectral power density (SPD) for periodicities between 1.5 and 1.9 years in Neptune's atmosphere against the same periodicity in Lyman alpha (UV) radiation, for Neptune lagging UV by 0-10 years. Dotted lines mark 95% confidence limits from multiple (10000) realisations of the SPDs calculated with the uncertainties in the magnitude fluctuations. (b) Average Neptune 472nm SPD against UV SPD data values for the 1.5-1.9 year periodicity, with Neptune lagging UV by 4 years. The filled circles are from 1980-1989, when the 1.5-1.9 year periodicity in GCR was particularly strong, and the rest of the data are open circles. A lowess fit to all the data points is also shown (solid line).

Figure 7 Comparison of smoothing approaches for Neptune magnitude time series data. (a) Raw data are shown as points (blue squares for 472nm, green circles for 551nm), with three different smoothing lines as indicated on the legend (b) fluctuations calculated using the three different fits, with the same lines as indicated in the legend for (a).

Figure 8 Saturation ratios required for condensation onto ions, for (a) methane at 66K and (b) diacetylene (butadiyne) at 100K. The critical saturation ratio required is reduced if the ions are multiply charged, with calculations given for 1, 2 and 5 elementary charges *e*.

Tables

Case	Physical interpretation	Coefficients in equation (1)	Adjusted coefficient of determination (R^2) *and statistical significance p*	
			y (551nm)	*b* (472nm)
1	GCR only (ion-particle attachment limited)	κ=0, μ=0; λ free to vary	0.02	0.13 *(p<0.01)*
2	√GCR only (ion-ion/ion-electron recombination limited)	κ=0, λ=0; μ free to vary	0.02	0.13 *(p<0.01)*
3	GCR + √GCR	κ=0, λ and μ free to vary	0.03	0.12 *(p<0.05)*
4	UV only	λ=0, μ=0; κ free to vary	0.08 *(p<0.05)*	0.20 *(p<0.01)*
5	UV + GCR	μ=0; κ and λ free to vary	0.08 *(p<0.05)*	0.18 *(p<0.1)*
6	UV+ √GCR	λ=0; κ and μ free to vary	0.07 *(p<0.1)*	0.18 *(p<0.1)*
7	UV + GCR + √GCR	κ, λ and μ free to vary	0.14 *(p<0.05)*	0.19 *(p<0.05)*

Table 1 Summary of multiple regression analysis. Fits are weighted according to the errors on the measurements[3]. Statistical significances of the fits are indicated where better than 90% (p<0.1). The adjusted coefficient of determination (R^2) gives the fraction of the variance explained by the fit, whilst accounting for the different number of variables in each fit.

	Lowess	Loess	Quadratic
Lowess		**0.436**	**0.292**
Loess	**0.292**		0.035
Quadratic	**0.064**	0.009	

Table 2 *p* values obtained from Kolmogorov Smirnov tests of Neptune magnitude fluctuations detrended using three different techniques. If p>0.05 the data are not statistically "different" from each other, indicated in bold. The *b* 472 nm data are shown bottom left and the *y* 551 nm data are shown top right.

Quantity and description	**Value used (SI units)**	**Comment**
c_v specific heat of background gas at constant volume	2.07 x 10^{-23} J kg^{-1} K^{-1}	Assumes no modes are excited at these temperatures, so $3/2k_B$ (where k_B is the Boltzmann constant) (e.g. [42])
D diffusion coefficient	3 x 10^{-5} m^{2}s^{-1}	at 90K (methane diffusing in methane)[43]
$e_s(T)$ saturation vapour pressure	1.03 Pa	Calculated at 75K[9]
K thermal conductivity	0.509 W m K^{-1}	at 73.2K and 1013hPa[44]
L latent heat of vaporisation	5.1x10^5 J kg^{-1}	at 110K[45]
R' gas constant (background)	4.124x10^3 J kg^{-1} K^{-1}	Calculated from universal gas constant and molecular mass
R_v gas constant (condensing species)	5.183x10^2 J kg^{-1} K^{-1}	
r radius	Initial value 1 nm	
P pressure	1.1x10^5 Pa	Conditions defined in [9]
S supersaturation	2.7	
T temperature	75 K	
α coefficient	1	From [24]
β coefficient	0.04	
ρ_v density of condensing species	471 kg m^{-3}	Calculated at 75K [9]

Table 3 Quantities needed to estimate growth rate of methane droplets in hydrogen at approximately 100K

References

---

[1] Lockwood, G.W. and Thompson, D.T. Photometric variability of Neptune, 1972-2000, *Icarus,* **156**, 37-51, doi: 10.1006/icar.2001.6781 (2002)

[2] Lockwood G.W. and Jerzykiewycz M., Photometric variability of Uranus and Neptune, 1950-2004, *Icarus*, **180**, 442-452(2006)

[3] Lockwood G.W. *Photometry of Uranus and Neptune, 1972-2014*, unpublished document http://www2.lowell.edu/users/wes/index.htm (2015; accessed 26 June 2015)

[4] Fletcher, L. N., Drossart, P., Burgdorf, M., Orton, G. S., and Encrenaz, T., Neptune's atmospheric composition from AKARI infrared spectroscopy, *Astron. Astrophys.* **514**, A17 DOI: 10.1051/0004-6361/200913358 (2010)

[5] Karkoschka, E., Neptune's cloud and haze variations 1994–2008 from 500 HST–WFPC2 images, *Icarus* **2015**, 759-733, doi:10.1016/j.icarus.2011.06.010 (2011)

[6] Baines, K.H. and Smith, W.H., The atmospheric structure and dynamical properties of Neptune derived from ground-based and IUE spectrophotometry, *Icarus* **85**, 65-108 (1990)

[7] Lockwood, G.W. and Thompson, D.T., Long-term brightness variations of Neptune and the solar cycle modulation of its albedo, *Science*, **234**, 4783 1543-1545 (1986)

[8] Moses, J.I., Allen, M. and Yung, Y.L, Neptune's visual albedo variations over a solar cycle: A pre-Voyager look at ion-induced nucleation and cloud formation in Neptune's troposphere, *Geophys. Res. Lett.* **16***,* 12 1489-1492 (1989)

[9] Moses, J.I., Allen, M. and Yung, Y.L, Hydrocarbon nucleation and aerosol formation in Neptune's atmosphere, *Icarus* **99**, 318-346 (1992)

[10] Wilson, C.T.R., On a method of making visible the paths of ionising particles through a gas, *Proc. Roy. Soc. A*, **85**, 285-288 doi: 10.1098/rspa.1911.0041 (1911)

[11] Aplin, K.L., Atmospheric electrification in the Solar System, *Surv. Geophys.*, **27***,* 1, 63-108 doi: 10.1007/s10712-005-0642-9 (2006)

---

[12] Mironova, I.A. et al, Energetic Particle Influence on the Earth's Atmosphere, *Space Sci. Revs.*, **194**(1-4), 1-9 (2015)

[13] Valdés-Galicia, J. F., Pérez-Enríquez, R. and Otaoloa, J. A, The cosmic-ray 1.68 year variation: a clue to understand the nature of the solar cycle? *Solar Phys.* **167***,* 409–417 doi:10.1007/BF00146349 (1996)

[14] Harrison, R.G., Discrimination between cosmic ray and solar irradiance effects on clouds, and evidence for geophysical modulation of cloud thickness, *Proc. Roy. Soc. A.* **464**, 2575-2590 doi:10.1098/rspa.2008.0081 (2008)

[15] Harrison, R.G., Nicoll, K.A. and Aplin, K.L., Vertical profile measurements of lower troposphere ionisation, *J. Atmos. Solar-Terr. Phys*., **119**, 203-210 doi:10.1016/j.jastp.2014.08.006 (2014)

[16] Vaughan, S., *Scientific Inference: Learning from Data*, Cambridge, UK: Cambridge University Press, (2013)

[17] Pryor, W. R., and Hord, C. W., A study of photopolarimeter system UV absorption data on Jupiter, Saturn, Uranus, and Neptune: Implications for auroral haze formation. *Icarus*, **91**(1), 161-172 (1991)

[18] Kato, C., Munakata, K., Yasue, S., Inoue, K., and McDonald, F. B. A 1.7-year quasi-periodicity in cosmic ray intensity variation observed in the outer heliosphere, *J. Geophys. Res.,* **108** (A10), 1367, doi:10.1029/2003JA009897 (2003)

[19] Rouillard, A. and Lockwood, M., Oscillations in the open solar magnetic flux with a period of 1.68 years: imprint on galactic cosmic rays and implications for heliospheric shielding. *Ann. Geophys.* **22**, 4381–4395 (2004)

[20] Kane, R. P., Short-term periodicities in solar indices. *Solar Phys.* **227**, 155–175, doi:10.1007/s11207-005-1110-x (2005)

[21] Harrison, R.G. and Maercz F., Heliospheric timescale identified in surface atmospheric electricity. *Geophys. Res. Lett*, **34**. L23816 doi: 10.1029/2007GL031714 (2007)

---

[22] Krimigis, S.M., et al The Low Energy Charged Particle (LECP) experiment on the Voyager spacecraft, *Space Sci. Rev,* **21**, 3, 329-354 (1977)

[23] Stone, E.C. and Miner, E.D., The Voyager 2 encounter with the Neptune system, *Science* **246**, 4936, 1417-1421 (1989)

[24] Rogers, R.R. and Yau, M.L., *A Short Course in Cloud Physics*, 3rd edition, Oxford, UK: Pergamon Press (1989)

[25] Clement, C. F., and Harrison, R. G. The charging of radioactive aerosols. *J. Aerosol Sci*, **23**(5), 481-504. (1992)

[26] Stoker, C.R. and Toon, O., Moist convection on Neptune, *Geophys. Res. Letts.* **16**, 8, 929-932 (1989)

[27] Hammel H.B. and Lockwood G.W. (2007) Long-term atmospheric variability on Uranus and Neptune, *Icarus* 186, 291-301

[28] Cleveland, W. S. (1981) LOWESS: A program for smoothing scatterplots by robust locally weighted regression *The American Statistician* 35, 54.

[29] Cleveland W. S., Grosse E. and Shyu W. M. (1992) *Local regression models*. In: Statistical Models in S (eds J.M. Chambers and T.J. Hastie) Pacific Grove, CA: Wadsworth & Brooks/Cole.

[30] Crawley M.J. (2005), *Statistics: an introduction using R*, Chichester, UK: Wiley

[31] Nakamura, K. *et al* (Particle Data Group) Review of particle physics (section 24: Cosmic rays) *J. Phys. G: Nucl. Part. Phys.* **37** 075021 (2010)

[32] Usoskin, I.G., Mursula, K., Kangas, J. and Gvozdevsky, B. On-line database of cosmic ray intensities, *Proc. Int. Cosmic Ray Conf.* 2001 2-4 (2001)

[33] Stone, E.C., et al, Cosmic ray investigation for the Voyager missions: energetic particle studies in the outer heliosphere - and beyond, *Space Sci. Rev.*, **21**, 355 (1977)

[34] Lean, J.L. and Skumanich, A., Variability of the Lyman alpha flux with solar activity, *J. Geophys. Res.*, **88**, A7, 5751-5759 (1983)

---

[35] Woods, T.N., Tobiska, W.K, Rottman, G.J., and Worden, J.R., Improved solar Lyman alpha irradiance modelling from 1947 through 1999 based on UARS observations, *J. Geophys. Res.* **105**, A12, 27195-27215 (2000)

[36] Lomb, N.R. Least squares frequency analysis of unequally spaced data, *Astrophys. Space Sci.* **39***,* 447–462, doi: 10.1007/BF00648343 (1976)

[37] Scargle, J.D., Studies in astronomical time series analysis. II - Statistical aspects of spectral analysis of unevenly spaced data, *Ap. J*, **263**, 835-853 (1982)

[38] Press, W.H. and Rybicki, G.B., Fast Algorithm for Spectral Analysis of Unevenly Sampled Data, *Ap. J.*, **338**, 277-280 (1989)

[39] Eyer, L. and Bartholdi, P., Variable stars: Which Nyquist frequency? *Astron. Astrophys. Supp. Ser.*, **135**, 1 (1999)

[40] Koen, C., The Nyquist frequency for irregularly spaced timeseries: a calculation formula, *Mon. Not. R. Astron. Soc.* **371**, 1390-1394 doi:10.1111/j.1365-2966.2006.10762.x (2006)

[41] Duchon, C.E., Lanczos Filtering in One and Two Dimensions. *J. Appl. Meteor.*, **18**, 1016–1022. doi: 10.1175/1520-0450(1979)018<1016:LFIOAT>2.0.CO;2 (1979)

[42] Blundell S.J. and Blundell K.M. *Concepts in Thermal Physics*, Oxford, UK: Oxford University Press (2006)

[43] Winn E.B. The temperature dependence of the self-diffusion coefficients of argon, neon, nitrogen, oxygen, carbon dioxide and methane, *Phys. Rev.* 80, 6, 1024 (1950)

[44] Kaye G.W.C. and Laby T.H., *Tables of physical and chemical constants*, London, UK: Longman, 16th edition (1995)

[45] Lide D.R. (ed) (1995) *CRC handbook of chemistry and physics*, London, UK: CRC Press, 76th edition