New Insights into Cosmic-Ray-induced Biosignature Chemistry in Earth-like Atmospheres

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Abstract

With the recent discoveries of terrestrial planets around active M-dwarfs, destruction processes masking the possible presence of life are receiving increased attention in the exoplanet community. We investigate potential biosignatures of planets having Earth-like (N2–O2) atmospheres orbiting in the habitable zone of the M-dwarf star AD LEO. These are bombarded by high energetic particles that can create showers of secondary particles at the surface. We apply our cloud-free 1D climate-chemistry model to study the influence of key particle shower parameters and chemical efficiencies of NOx and HOx production from cosmic rays. We determine the effect of stellar radiation and cosmic rays upon atmospheric composition, temperature, and spectral appearance. Despite strong stratospheric O3 destruction by cosmic rays, smog O3 can significantly build up in the lower atmosphere of our modeled planet around AD LEO related to low stellar UVB. The abundance of N2O decreases with increasing flaring energies but a sink reaction for N2O with excited oxygen becomes weaker, stabilizing its abundance. CH4 is removed mainly by Cl in the upper atmosphere for the strong flaring cases and not via hydroxyl as is otherwise usually the case. Cosmic rays weaken the role of CH4 in heating the middle atmosphere so that H2O absorption becomes more important. We additionally underline the importance of HNO3 as a possible marker for strong stellar particle showers. In a nutshell, uncertainty in NOx and HOx production from cosmic rays significantly influences the abundance of biosignatures and spectral appearance.

Key words: astrobiology – astrochemistry – methods: numerical – planets and satellites: atmospheres – planets and satellites: terrestrial planets – planet–star interactions

1. Introduction

Cool M-dwarf stars are favored targets in exoplanetary sciences due to their high abundance in the solar neighborhood, a close-in habitable zone (HZ), hence short orbital periods, and a high planet/star contrast. For an overview see, e.g., Kasting et al. (1993); Scalo et al. (2007); and Shields et al. (2016). There are however drawbacks. Planets lying in the close-in HZ could be tidally locked (e.g., Kasting et al. 1993; Selsis 2000) and could be bombarded by high levels of energetic particles (Grießmeier et al. 2005). An additional drawback for M-star planet habitability is the long, bright, pre-main-sequence phase of the parent star, which may devolatilize planets that would later reside in their HZs (e.g., Ramirez & Kaltenegger 2014; Luger & Barnes 2015; Tian & Ida 2015). Nevertheless, planets in the HZ of M-dwarf stars could represent the first opportunity to detect atmospheric properties and even biosignatures of rocky extrasolar planets. There are numerous relevant model studies, e.g., in 1D (Segura et al. 2003, 2005, 2010; Grenfell et al. 2012; Kopparapu et al. 2013; Rugheimer et al. 2015b; Tabataba-Vakili et al. 2016) and in 3D (Leconte et al. 2013; Shields et al. 2013, 2016; Yang et al. 2014; Godolt et al. 2015; Kopparapu et al. 2016). Interpretation of such potential future observation heavily relies on our detailed understanding of atmospheric physical, chemical, and biological processes and their interaction with different electromagnetic radiation and high energetic particles (HEPs), such as galactic cosmic rays (GCRs) and stellar energetic particles (SEPs). The latter has received only limited attention in the exoplanet community so far. Our general understanding of the redistribution of incoming HEPs into secondary particles in so-called air showers through the atmosphere and their influence upon atmospheric chemistry dates back to theoretical work done in the early 1980s (Rusch et al. 1981; Solomon et al. 1981). A more recent study by Airapetian et al. (2016) investigated the production of N2O via SEPs for the early Earth. While our own star is comparably quiescent, many M-dwarfs show high activity, in which flares with energies comparable to the devastating Carrington event on Earth in the nineteenth century regularly occur up to a few times a day and orders of magnitude higher energetic events have been observed, e.g., for the herein studied M-dwarf AD LEO (Hawley & Pettersen 1991; Atri 2017).

Recently, potentially Earth-like planets have been found in the HZ around M-dwarfs (Proxima Cen b, LHS1140 b, and TRAPPIST-1 d-f), which may be studied in further detail with upcoming instrumentation on, e.g., the James Webb Space Telescope (JWST; Gardner et al. 2006) and E-ELT (Kasper et al. 2010). The impact of HEPs upon atmospheric chemistry needs further investigation. HEP-induced ion pairs react with molecular oxygen, molecular nitrogen, and water to cascade into nitrogen oxides (NOx = N+NO+NO2+N3) and hydrogen oxides (HOx = H+HO+HO2) (Porter et al. 1976; Rusch et al. 1981; Solomon et al. 1981). NOx and HOx catalytically destroy ozone (O3) in the lower and upper stratosphere respectively (Crutzen 1970) but can form O3 in the troposphere due to the so-called smog mechanism (Haagen-Smit 1952). They are stored and released from reservoir molecules such as HNO3, depending on, e.g., UV radiation and temperature. Recent model studies have shown that HEP-induced NOx and HOx from particle showers can indeed significantly reduce O3 in an Earth-like atmosphere (Grenfell et al. 2012; Grießmeier et al. 2016). This work focuses on detecting N2O and HOx production from cosmic rays as potential biosignatures of Earth-like planets orbiting M-dwarf stars. We carried out model calculations using our cloud-free 1D climate-chemistry model to study their effect on atmospheric composition, temperature, and spectral appearance.
et al. 2016; Tabataba-Vakili et al. 2016). Production rates of around 1.27 NOx (Porter et al. 1976; Rusch et al. 1981) and 2.0 HOx (Solomon et al. 1981) per ion pair have been assumed in numerous atmospheric studies, but recent ion-chemistry studies by, e.g., Sinnhuber et al. (2012) and Verronen & Lehmann (2013) have pointed out that the uncertainties in these complex chemical coupling coefficients might be underestimated, especially when additionally taking into account negative ion chemistry. When conducting numerical studies of rocky planets chemical coupling coefficients might be underestimated, especially when additionally taking into account negative ion chemistry. When conducting numerical studies of rocky planets around active M-dwarfs, such uncertainties can have a major impact on atmospheric abundances, including species influenced by biogenic processes. O3, for example, is removed catalytically by HOx and NOx. Also, CH4 is usually removed by OH, a member of the HOx family.

Based on the above, the main motivation of this work is to compare the influence of different M-dwarf stellar flaring energies to that of the uncertainties in atmospheric NOx–HOx production efficiencies from incoming SEPs and show their impact on overall climate and spectral features in transit observations. In Section 2 we describe the models used for this work and motivate the modeled scenarios. In Section 3 we briefly describe our results, before discussing and comparing them to other relevant works in Section 4. Finally, in Section 5 we draw our conclusions.

2. Modeling Framework

2.1. Model Description

We investigate the influence of GCRs and SEPs from quiescent and flaring stars on atmospheric chemistry and potential biosignatures like O3, nitrous oxide (N2O), CH4, and chloromethane (CH3Cl). We build upon our stationary, global mean, cloud-free coupled climate-chemistry 1D model (Tabataba-Vakili et al. 2016), and update the cosmic rays’ propagation. First we compute the fluxes of primary HEps, either GCRs or SEPs, that arrive at the top of our model atmosphere (TOA) at 6.6 Pa, using the magnetospheric model from Grießmeier et al. (2005, 2009). For Earth reference cases we take GCR and SEP measurements outside the Earth’s magnetic field for solar minimum conditions and use cutoff energies from Grießmeier et al. (2016) for the Earth’s magnetic shielding. For exoplanet runs we assume the same planetary magnetic field, but scale the HEP fluxes in all energy ranges as follows. For SEPs we use a simplified (conservative) inverse squared scaling with distance from the star (see Grenfell et al. 2012), hence neglect possible magnetic diffusion processes in the heliosphere, which would further increase the power-law exponent beyond 2.0 in the scaling of HEP fluxes for short-period orbits. We partly compensate for this effect with higher intrinsic HEP flux scenarios from the star (see model scenarios). For GCRs at exoplanets we adopt enhanced shielding modulation closer to the star, as described by Grießmeier et al. (2009). Once we have the TOA HEP fluxes, we use the Gaisser–Hillas approach (see, e.g., Tabataba-Vakili et al. 2016) to calculate the atmospheric ion-pair production profiles (Q). In the case of the Earth, we can compare our approach to more sophisticated models like, e.g., the PLANETOCOSMICS Monte Carlo simulations of the cosmic-ray-induced secondary-particle showers performed by the Christian-Albrechts University (CAU) in Kiel, Germany (Fichtner et al. 2013), and find them to be in qualitatively good agreement, as shown in Figure 1. Consequently, these ion pairs cascade into NOx and HOx species. The NOx–HOx production efficiencies describing how many NOx and HOx are subsequently produced per cosmic-ray-induced ion pair are widely used in ion-chemistry models with values that were calculated by Rusch et al. (1981) and Solomon et al. (1981). These values are based on an Earth atmospheric composition assuming ionization to be directly proportional to ionization cross sections, which themselves are taken to be independent of pressure and temperature. Note that negative ion chemistry was taken into account much later by Verronen & Lehmann (2013), which further influences the NOx–HOx production efficiencies. In our study we made the cosmic-ray air-shower parameters in our climate-chemistry model flexible so that we could analyze the influence of the uncertainties of these chemical production efficiencies fNOx and fHOx on potential biosignatures compared with the impact of potential stellar flaring scenarios.

Lastly, transit spectra, i.e., transmission spectra (T(λ)) are calculated using the "Generic Atmospheric Radiation Line-by-line Infrared Code" GARLIC (Schreier et al. 2014) that has been extensively verified (e.g., Schreier et al. 2018a) and validated (Schreier et al. 2018b), a FORTRAN90 version of MIRART/SQUIRRL (see, e.g., von Clarmann et al. 2003; Melsheimer et al. 2005) used by (e.g., Rauer et al. 2011; Grießmeier et al. 2016; Tabataba-Vakili et al. 2016). In this study we use GARLIC with HITRAN2012 (Rothman et al. 2013) along with the “CKD” continua (Clough et al. 1989) for calculations of line absorption and Rayleigh scattering parameterization from Sneep & Ubachs (2005),
Marcq et al. (2011), Murphy (1977). We use temperature, pressure, water vapor, and concentration profiles of those species (23 in total\(^4\)), which are present in both HITRAN2012 as well as in our climate-chemistry model. The corresponding transit depths \(\delta(\lambda)\) are calculated using:

\[
\delta(\lambda) = \left(\frac{r_p + h(\lambda)}{r_s}\right)^2,
\]

where \(r_p\) is the planetary radius, \(r_s\) the stellar radius, and

\[
h(\lambda) = \sum_i (1 - T_i(\lambda)) \Delta h_i
\]

is the effective height of the atmosphere for a given wavelength.

2.2. Model Scenarios

In this study we focus on virtual Earth-like planets around the active red M4.5 dwarf star AD Leonis, hereafter AD LEO. In doing so, we place a virtual Earth (1 g planet, 1 atm surface pressure, albedo of 0.21—tuned to obtain global mean surface temperatures of 288.15 K on Earth) in the HZ around AD LEO in two different positions, starting with the Earth US standard 1976 reference atmosphere (COESA) and allow the climate and chemistry to relax into a new steady-state solution. First we start with an Earth around the Sun reference case, using the incoming stellar electromagnetic flux based on Gueymard (2004). To be comparable to earlier studies we next place the planet at a distance of 0.153 au around AD LEO, where the total stellar irradiance (TSI) equals the amount the Earth receives from the Sun before moving it further outward to 0.161 au (0.9 TSI\(_{\oplus}\)) around AD LEO where it receives only 90\% of the Earth’s TSI. In all AD LEO cases we use the electromagnetic spectrum based on Segura et al. (2005). The former approach of 1.0 TSI\(_{\oplus}\) together with an Earth-like relative humidity profile (Manabe & Wetherald 1967) leads to surface temperatures larger than 288 K (see also the scaling arguments in Segura et al. 2003 and references therein). Various modeling studies, including early 1D studies (e.g., Cess 1976; Kasting & Ackerman 1986), as well as more recent 3D studies (e.g., Leconte et al. 2013; Popp et al. 2015; Godolt et al. 2016; Fujii et al. 2017) have argued that for increased surface temperatures the relative humidity profile may differ from that of the Earth (e.g., Manabe & Wetherald 1967), which we use here and has also been assumed in previous studies (Segura et al. 2010; Rauer et al. 2011; Grenfell et al. 2012; Rugheimer et al. 2015a). Other studies, e.g., Kasting et al. (1993) and Kopp et al. (2013), assumed a fully saturated atmosphere and found that an Earth-like planet around AD LEO would be close to or even inside the inner edge of the HZ. This assumption of a fully saturated atmosphere may however overestimate the water concentrations, as shown by 3D studies, see, e.g., Leconte et al. (2013), Yang et al. (2014), and Kopp et al. (2016). The 3D modeling results by Shields et al. (2013) show that an Earth-like planet around AD LEO receiving 90\% insolation may have similar surface temperatures as the Earth around the Sun. Hence, for this case, the assumption of an Earth-like relative humidity profile to determine the water profile in the 1D model seems to be better justified and in line with 3D model results (see, e.g., Godolt et al. 2016). Whereas the approach of placing the planet at 0.161 au (0.9 TSI\(_{\oplus}\)) around AD LEO is model dependent, it has the advantage of lying closer to Earth conditions, where our model is validated.

For each of the above cases we investigate various stellar activity scenarios for the HEP shower through the atmosphere, all based on measurements on Earth, and scaled for AD LEO according to the abovementioned functions. We start with the GCR and SEP stellar-minimum background cases, as described above. Then we compare various stellar flaring scenarios, all based on GOES 6 and 7 measurements of the medium-hard spectrum flare that hit the Earth in 1989 (Smart & Shea 2002), hereafter SPE89. We assume quasi-constant flaring conditions, i.e., a flaring frequency faster than the relevant chemical response timescales to investigate long-term climate and composition effects of such violent environments rather than short-term variations. We justify our assumption because, e.g., the Earth’s mean O\(_3\) column does not change significantly with the day–night cycle, whereas flaring on AD LEO has been extensively measured to be in the order of a few per day, with event energies exceeding those of the largest recorded events on Earth (∼10\(^{32}\) erg; Atri 2017). Additionally, from the Kepler survey we have multiple M-star observations with flaring energies of up to 10\(^{30}\) erg and frequencies of up to 100 times those of G-stars (Maehara et al. 2012; Shibayama et al. 2013; Candelaresi et al. 2014). With this in mind, we model higher flaring scenarios by multiplying the SPE89 particle fluxes in all energy ranges by 10, 50, and 100. For AD LEO runs this adds to the (∼40×) enhanced flux density due to proximity to the host star. This means that our virtual Earth at a distance of 0.153 au around an AD LEO flaring with 100 times enhanced SPE89 strength, hereafter SPE89x100, actually receives 4,272 times the SEP flux than Earth received during SPE89. For comparison we also investigated an Earth in its current position receiving the same SEP flux densities and added these three scenarios as separate cases only for the Earth around the Sun cases, flaring with SPE89x427, SPE89x2136, and SPE89x4272 to compare with the AD LEO SPE89x10, SPE89x50, and SPE89x100 cases, respectively.

Lastly, for all of the above scenarios, we perform our parameter study and vary the NOx–HOx production efficiencies per cosmic-ray-induced ion pair (\(\bar{Q}\)) within their plausible parameter ranges (Rusch et al. 1981; Solomon et al. 1981; Sinnhuber et al. 2012; Verronen & Lehmann 2013) for every combination of \(f_{\text{NOX}} = [1.0, 1.27, 1.44, 1.6, 2.0]\) and \(f_{\text{HOx}} = [0.0, 1.0, 2.0]\). The full set of model scenarios can be seen in Table 1.

We would like to remark that in the thought experiment of an Earth-like planet around AD LEO we assume that life would still be present in the form of biogenic surface emissions as on Earth even in the highest flaring cases, despite the hostility from its host star. Also we assume Earth’s evolutionary history, and a mean global daytime average, which might not strictly hold in the case of tidal locking. We do this for the sake of simplicity to study the impact of HEPs alone.

3. Results

Figure 2 shows the atmospheric temperature profiles for our three planetary positions, the Earth around the Sun (black line), the virtual Earth around AD LEO at a distance of 0.153 au with a TSI = 1.0 TSI\(_{\oplus}\) (red line), and the virtual Earth around AD LEO at 0.161 au with a TSI = 0.9 TSI\(_{\oplus}\) (blue line), all with a scaled GCR background. The reference is always the GCR background, but a solar minimum SEP background leads to
indistinguishable results for our analysis and is therefore not shown in this work. Until stated otherwise, we show results for the chemical air-shower production efficiencies $f_{NOx}$ and $f_{HOx}$ are the chemical air-shower production efficiencies for NOx and HOx production per ion pair, respectively, studied for each configuration.

Table 1: Model Scenarios in This Work

| Star  | Distance [au] | HEPs     | $f_{NOx}$ | $f_{HOx}$ |
|-------|---------------|----------|-----------|-----------|
| Sun   | 1.0           | GCR      | 1.0       | 0.0       |
|       |               | SEP      | 1.27      | 0.0       |
|       |               | SPE89    | 1.0       | 0.0       |
|       |               | SPE89x10 | 1.27      | 0.0       |
|       |               | SPE89x50 | 1.44      | 1.0       |
|       |               | SPE89x100| 1.6       | 2.0       |
|       |               | SPE89x427| 2.0       | 0.0       |
|       |               | SPE89x2136|        |           |
|       |               | SPE89x4272|        |           |
| AD LEO | 0.153        | GCR      | 1.0       | 0.0       |
|       | 0.161         | SEP      | 1.27      | 0.0       |
|       |               | SPE89    | 1.44      | 1.0       |
|       |               | SPE89x10 | 1.6       | 2.0       |
|       |               | SPE89x50 | 2.0       | 0.0       |

Note. “Star” indicates here the host star of our planet, “distance” shows the orbital distance of our planet to its host star, and “HEP” is the energetic particle bombardment on our planet. $f_{NOx}$ and $f_{HOx}$ are the chemical air-shower production efficiencies for NOx and HOx production per ion pair, respectively, studied for each configuration.

![Figure 2](image2.png)

**Figure 2.** Temperature profiles for the Earth around the Sun case (black line), the Earth around AD LEO at a distance of 0.153 au where TSI = 1.0 TSI$_{\oplus}$ (red line), and the Earth around AD LEO at 0.161 au or 0.9 TSI$_{\oplus}$ (blue line), all with a GCR background.

![Figure 3](image3.png)

**Figure 3.** Atmospheric column amounts for O$_3$, N$_2$O, CH$_4$, and CH$_3$Cl presented in Dobson units (1 DU = 2.687 × 10$^{16}$ molec. cm$^{-2}$) for the Earth around the Sun (top), the Earth around AD LEO at TSI = 1.0 TSI$_{\oplus}$ (middle), and the Earth around AD LEO at 0.9 TSI$_{\oplus}$ (bottom) cases. In each panel we show model runs for the GCR background (black), stellar flaring scaled from the SPE89 on Earth (green), and the enhanced flaring runs SPE89 multiplied by 10 (orange), 50 (blue), and 100 (red). All particle fluxes received by the planet are scaled from the observed value (at 1 au) to the appropriate planetary orbital distance. The results for the solar minimum SEP background are indistinguishable from the GCR background, and therefore are not shown. The upper panel additionally shows the three cases (SPE89x427 yellow), SPE89x2136 (cyan), and SPE89x4272 (magenta) where the Earth around the Sun case would receive the same SEP flux density from the Sun as the Earth around AD LEO at TSI = 1.0 TSI$_{\oplus}$ (middle panel) receives from an AD LEO flaring scaled from SPE89x10 (orange), SPE89x50 (blue), and SPE89x100 (red) strength, respectively (see Section 2 for further explanation).
strength the O$_3$ column is depleted, similar to results of, e.g., Grenfell et al. (2012) and Tabataba-Vakili et al. (2016). The same holds qualitatively for N$_2$O although note that we calculate here a “saturation” behavior, i.e., where increasing flaming energy has no further effect upon the N$_2$O column. Both the CH$_4$ and CH$_3$Cl columns also follow the same trend of depletion, e.g., from $\sim$1.6 ppmv Earth tropospheric CH$_4$ concentrations down to $\sim$0.2 ppmv of tropospheric CH$_4$ in the SPE89x100 case. An exception presents the interesting increase in CH$_4$ and CH$_3$Cl for our most active Sun cases (upper panel), SPE89x2136 (cyan) and SPE89x4272 (magenta), which were added for comparison purposes with the AD LEO cases and which we will discuss in Section 4. When we compare the GCR background runs for the Earth around the Sun case with the AD LEO case, we see an increase of two orders of magnitude in the CH$_4$ and CH$_3$Cl column amounts around AD LEO due to slower O$_3$ photolysis resulting in lower OH densities, as discussed in Segura et al. (2005).

In order to investigate the column behavior in Figure 3, Figure 4 shows the atmospheric profiles in molecules cm$^{-3}$ in the case of our virtual Earth around AD LEO at 1.0 TSI$\odot$ as shown in Figure 3 (middle panel) and by the red line in Figure 2. The ozone profile (upper left), N$_2$O (upper right), methane (lower left), and CH$_3$Cl profile (lower right) are each compared for the different flaming scenarios from Figure 3 (middle).

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In order to investigate the column behavior in Figure 3, Figure 4 shows the atmospheric profiles in molecules cm$^{-3}$ in the case of our virtual Earth around AD LEO at 1.0 TSI$\odot$ as shown in Figure 3 (middle panel). The color coding for different flaming strengths is the same as shown in Figure 3. We calculate the stratospheric ozone loss (upper left) with the increasing influx of SEPs, compared with a quiescent AD LEO (black line), as well as increased ozone in the troposphere, which is discussed in Section 4. The N$_2$O (upper right) on the other hand, responds only weakly to increasing flame strength, decreasing from $\sim$800 ppbv ($2 \times 10^{13}$ molec. cm$^{-3}$) (GCR case) to $\sim$250 ppbv ($9 \times 10^{12}$ molec. cm$^{-3}$) (SPE89x100) in the lower atmosphere. Methane and CH$_3$Cl (lower row) both feature lower concentrations throughout the whole atmosphere with increasing flame strength. The greatly enhanced surface concentration of $\sim$400 ppmv ($10^{16}$ molec. cm$^{-3}$) CH$_4$ and $\sim$200 ppbv (5 $\times 10^{12}$ molec. cm$^{-3}$) CH$_3$Cl in the AD LEO GCR case (compared with $\sim$1.6 ppmv (3.9 $\times 10^{13}$ molec. cm$^{-3}$) CH$_4$ and $\sim$0.5 ppbv (1.2 $\times 10^{10}$ molec. cm$^{-3}$) CH$_3$Cl Earth tropospheric concentrations) decreases in our simulations down to $\sim$5 ppmv (10$^{14}$ molec. cm$^{-3}$) of CH$_4$ and $\sim$2 ppbv (4 $\times 10^{10}$ molec. cm$^{-3}$) CH$_3$Cl for the AD LEO SPE89x100 case.

In order to investigate the methane response, whose main sinks are OH (lower to mid atmosphere) and CI (upper atmosphere), we analyze chlorine containing species in our model atmospheres, as shown in Figure 5. For all our three planetary configurations we compare background GCR runs (black line) with the 50 times enhanced SPE89 flaring cases (blue line). The solid lines represent total chlorine (Cl$_t$), i.e., the sum of all chlorine-bearing species, which increases by two orders of magnitude in molecules cm$^{-3}$ when we go from the Earth to an Earth-like planet around AD LEO. For all cases the majority of stratospheric chlorine is in the form of HCl (dashed line), while in the upper stratosphere, atomic chlorine, Cl, also reaches significant levels above 40 km. This is the region where CH$_4$ production becomes controlled by CI (dashed–dotted line), instead of OH, which is the major methane destroying reaction below around 40 km, as discussed in Section 4. CIONO$_2$ (dotted line) is only the dominant chlorine-bearing species for a small fraction of the Earth’s mid-stratosphere for quiescent solar cases.

Figure 6 compares the influence of varying the chemical air-shower production efficiencies $f_{NOx}$ and $f_{HOx}$ for the different flaming cases for the Earth (top), the 1.0 TSI$\odot$ AD LEO case (middle), and the 0.9 TSI$\odot$ AD LEO case (bottom). We show the resulting ozone profiles (left), temperature (middle), and the UVB environment profile in W/m$^2$ (right). Shades of green represent the SPE89 flaring cases for different SEP-induced NOx–HOx production efficiencies; shades of orange represent the same runs for 10 times enhanced flaming; and shades of blue represent the 100 times enhanced flaming cases, respectively. Within the green, orange, and blue scenarios, the darkest colors represent the lowest parameter values $f_{NOx} = 1.0$ and $f_{HOx} = 0.0$, while the lightest colors represent the highest values of $f_{NOx} = 2.0$ and $f_{HOx} = 2.0$, with all other combinations in between. For all quiescent star (GCR) cases (black line) all modeled combinations of $f_{NOx}$ and $f_{HOx}$ result in virtually indistinguishable profiles, hence only the cases of $f_{NOx} = 1.27$ NOx/Q and $f_{HOx} = 2.0$ HOx/Q, as used by other works, are shown. For the Earth around the Sun case, the results suggest that the influence of changing the NOx–HOx production efficiencies is less important than varying the Sun’s flaring strength, i.e., the amount of incoming SEPs. In the AD LEO cases, on the other hand, $f_{NOx}$ and $f_{HOx}$ influence at least the atmospheric temperature and ozone profiles significantly, up to a point where for the 0.9 TSI$\odot$ case, a high flaring AD LEO (50 times enhanced SPE89) can lead to an atmospheric temperature profile similar to a quiescent AD LEO case, if the chemical air-shower parameters through the planet’s atmosphere are $f_{NOx} = 2.0$ and $f_{HOx} = 0.0$. In contrast with $f_{NOx} = 2.0$ and $f_{HOx} = 2.0$, the temperature may be reduced by up to 40 K throughout most of the stratosphere.

To investigate whether the abovementioned differences in stratospheric temperature and composition due to different NOx–HOx production efficiencies in the SPE89x50 strong flaring AD LEO cases with a planet at 0.9 TSI$\odot$ (bottom row of Figure 6) have any distinguishable effect on atmospheric spectra, Figure 7 shows the corresponding transit depths $\delta(\lambda)$.
The spectra are shown with constant spectral resolution $R = \lambda / \Delta \lambda = 100$ over the wavelength range of 0.3–30 $\mu$m. This corresponds to, e.g., one mode of the near-infrared spectrograph NIRSpec on board the upcoming JWST mission. We show the contribution of the planetary body, i.e., without the atmospheric contribution (dashed-black line), which we calculate to be 551.3 ppm. Similar to before, our reference case is the GCR background (black line) with $f_{\text{HOX}} = 1.27$ and $f_{\text{HOX}} = 2.0$, because runs for all the above described combinations of $f_{\text{HOX}}$ and $f_{\text{HOX}}$ for the GCR or SEP background cosmic rays result in qualitatively identical atmospheric concentration profiles for all our modeled molecules. First, we compare this to the SPE89x50 run for $f_{\text{HOX}} = 2.0$ and $f_{\text{HOX}} = 0.0$ (dashed-blue line), which results in an almost indistinguishable stratospheric temperature profile. We see the destruction of ozone due to flaring in the weakened 9.6 $\mu$m absorption band as well as reduced absorption by water and methane in the near-infrared (1–2 $\mu$m). We also see HNO$_3$ absorption above 10 $\mu$m becoming visible. The second comparison in Figure 7 is with the SPE89x50 run for $f_{\text{HOX}} = 2.0$ and $f_{\text{HOX}} = 0.0$ (light blue line). Here we see even stronger suppression of the near-infrared water and methane features, and even stronger HNO$_3$ absorption in the far-infrared. There are also new HNO$_3$ features visible around 17 and 21 $\mu$m. The 9.6 $\mu$m O$_3$ absorption band is a little less reduced than in the $f_{\text{HOX}} = 0.0$ case, due to NOX–HOx reactions, which limit the NOX sink for O$_3$, similar to Tabataba-Vakili et al. (2016). All three runs clearly show the slope due to Rayleigh scattering toward the visible and into the ultraviolet.

To further explain the differences in the transit spectra of Figure 7, Figure 8 shows the corresponding atmospheric profiles of temperature, O$_3$, CH$_4$, H$_2$O, N$_2$O, and HNO$_3$ for the three AD LEO runs at 0.9 TSI$_{\oplus}$ using the same color scheme (O$_3$ and temperature are also shown and explained in Figure 6).

Compared with the GCR case (black line) with a fairly constant CH$_4$ concentration of $\sim$500 ppmv ($1.3 \times 10^{16}$ molec. cm$^{-3}$) throughout our model atmosphere CH$_4$ is reduced throughout the whole atmosphere in both SPE89x50 cases, $f_{\text{HOX}} = 2.0$ and $f_{\text{HOX}} = 0.0$ (dashed-blue line), resulting in $\sim$60 ppmv ($1.4 \times 10^{15}$ molec. cm$^{-3}$) CH$_4$, and $f_{\text{HOX}} = 2.0$ and $f_{\text{HOX}} = 2.0$ (light blue) leaving $\sim$20 ppmv ($5 \times 10^{14}$ molec. cm$^{-3}$) CH$_4$.

The H$_2$O profiles show a similar behavior, although the H$_2$O abundance is clearly less affected by the HEPs in the SPE89x50 $f_{\text{HOX}} = 0.0$ case, with still $\sim$60–100 ppmv ($\sim10^{14}$ molec. cm$^{-3}$) in the mid and upper atmosphere than in the SPE89x50 $f_{\text{HOX}} = 2.0$ case leaving only $\sim$2–20 ppmv ($\sim2 \times 10^{12}$ molec. cm$^{-3}$) in the mid and upper atmosphere, similar to the respective temperature profiles. Again, N$_2$O shows only weak responses to both flaring and $f_{\text{HOX}}$ variation. The HNO$_3$ profiles in both SPE89x50 cases are greatly enhanced, as seen in the spectra in Figure 7. In the lower- and mid-stratosphere HNO$_3$ is further increased in the $f_{\text{HOX}} = 2.0$ case peaking at $\sim$8 ppmv ($2 \times 10^{13}$ molec. cm$^{-3}$), which is about 10,000 times the modern Earth’s atmospheric concentration compared with the $f_{\text{HOX}} = 0.0$ case resulting in only $\sim$90 ppbv ($\sim3 \times 10^{12}$ molec. cm$^{-3}$) HNO$_3$, which explains the additional spectral HNO$_3$ features in Figure 7.

### 4. Discussion

In this study we analyze how increased HEP fluxes associated with active M-stars like AD LEO, influence the atmospheric chemistry and climate of Earth-like planets in comparison to the impact of chemical production efficiencies. Our special focus lies on biosignatures, i.e., species which on Earth are associated with life. Our results in Figure 2 (red line) show that the surface temperature would increase by over 12 K on placing a virtual Earth-like planet at 1.0 TSI$_{\oplus}$ around AD LEO when assuming an Earth-like relative humidity profile. However, such a temperature increase would likely change the hydrological cycle leading to a strong water feedback, as shown for a planet around K-stars by Godolt et al. (2015). This could place such planets outside the HZ as suggested by, e.g., Kopparapu et al. (2013). Assuming a planet around AD LEO that receives only 90% TSI$_{\oplus}$ (blue line), we obtain a moderate surface temperature of 289 K, which is in good agreement with the 3D model results of Shields et al. (2013).

The results for different flaring strengths of the same star (Figure 3) suggest stratospheric O$_3$ destruction with increasing HEP fluxes due to increased catalytic destruction from mainly NOx. All our runs for the Sun and AD LEO cases show this trend. As indicated in Figure 6, the effect of increasing flaring energy upon O$_3$ is different for the Earth, compared with an Earth-like planet around AD LEO. While the Earth would moderately lose O$_3$ in the troposphere and stratosphere, around AD LEO the impact on stratospheric O$_3$ is much fiercer, while in the troposphere the enhanced smog O$_3$ from NOx (see
Figure 9 for smog $\text{O}_3$ together with much lower stellar UVB input, i.e., less tropospheric $\text{O}_3$ destruction by photolysis, leads to enhanced tropospheric $\text{O}_3$ abundance. This behavior was confirmed by a detailed analysis of reaction rates of sources and sinks and related pathways. For a theoretically flaring Sun lower stratospheric $\text{O}_3$ abundance yields higher UVB radiation in the troposphere, i.e., higher tropospheric $\text{O}_3$ photolysis rates, limiting the smog $\text{O}_3$ build-up. For AD LEO the much lower UVB radiation cannot impact tropospheric smog $\text{O}_3$ build-up efficiently. In the high flaring cases of each host star, however,
The main sink for nitrous oxide (N$_2$O) is photolysis, which is generally much slower than O$_3$ photolysis. Despite decreased O$_3$ for increasing flare energies (Figures 3 and 4), increased UVB, N$_2$O values nevertheless appear to “saturate.” We can further see this in the UVB profiles in Figure 6: where stratospheric O$_3$ is significantly reduced, UVB absorption in the stratosphere is negligible. The dependence on O$_3$ is clearly visible in the AD LEO cases between 18 and 20 km, where O$_3$ shows a strong decrease with height. Only the increase in atmospheric density in the troposphere leads to a significant UVB absorption, where the abundance of O$_3$ is low. N$_2$O is never significantly destroyed by UVB in our study, even where O$_3$ is least abundant across all our model runs. N$_2$O photolysis is already slower in the stratosphere than O$_3$ photolysis. Additionally eddy diffusion might redistribute N$_2$O faster than it is photolytically destroyed by UVB and the N$_2$O reaction with O(1D) becomes O(1D) starved and hence is significantly reduced where O$_3$ abundance is lower. Such effects together may explain the N$_2$O behavior over a wide variety of flaring conditions. See Figure 9 for an overview.

Due to the direct increase of OH (an important CH$_4$ sink), one would also expect a steady reduction of CH$_4$ with increasing flare intensity (see Figure 3). For the AD LEO cases this holds, but for the high flaring Sun cases we see a turning point, above which CH$_4$ becomes more abundant again. This is a result of decreased OH production. In the troposphere and up to the mid-stratosphere, OH is the main sink of CH$_4$. Above that, direct reaction with chlorine becomes the dominant contribution, at least for the stellar flaring cases. This effect contributes only weakly to the total column amount, however, because of the low number density. In the troposphere, where most of the methane lies, OH is produced by three main sources, the reaction of O(1D) with H$_2$O, NO reacting with HO$_2$, and the lesser studied photolysis of HNO$_2$ (see Grenfell et al. 1995), which becomes dominant in the lower stratosphere (this requires future work). O(1D) itself is formed almost entirely from O$_3$ photolysis. With higher flaring and hence reduced ozone levels, there is a tipping point, where less O(1D) produced from O$_3$ leads to a reduction in OH. The same also happened in the AD LEO runs, but at higher flaring strengths of around 200 times enhanced SPE89 SEP fluxes, due to increased levels of smog O$_3$ and lower UVB radiation coming from AD LEO resulting in lower OH production, i.e., CH$_4$ destruction. Chloromethane, in all cases, follows the methane trends, only with smaller molecular abundance.
While the effect of varying $f_{\text{NOx}}$ and $f_{\text{HOx}}$ is rather weak for the Earth around the Sun case, even for an artificially high flaring Sun, the effect of varying these parameters for the AD LEO cases becomes very important. The lower row of Figure 6 for a virtual Earth around AD LEO at a distance of 0.161 au, i.e., 0.9 TSI$_{\odot}$, shows in the high flaring SPE89x50 case that especially varying $f_{\text{HOx}}$ can result in temperature differences throughout most of the stratosphere of around 40 K. Interestingly, the parameter combination of $f_{\text{NOx}} = 2.0$ and $f_{\text{HOx}} = 0.0$ around a high flaring AD LEO leads to a temperature profile similar to a quiescent AD LEO, while stratospheric ozone abundance in this case is significantly lower (up to four orders of magnitude) than in the quiescent AD LEO cases. O$_3$ is known to drive the stratospheric temperature inversion in the Earth’s atmosphere, but we would like to note here that for low stratospheric O$_3$ abundance caused by stellar flaring, i.e., reduced or complete lack of temperature inversion, other molecules such as CH$_4$ and H$_2$O determine stratospheric temperatures, as already discussed by, e.g., Segura et al. (2005), Rauer et al. (2011), Tabataba-Vakili et al. (2016). We see the main contribution to stratospheric heating in our model from the absorption of incoming stellar photons in the near-infrared range between 1 and 2 μm. As indicated in the transmission spectra in Figure 7 the H$_2$O and CH$_4$ bands have overlapping contributions and are therefore hard to distinguish. However, in contrast to the studies mentioned above, in our study of $f_{\text{NOx}}$ and $f_{\text{HOx}}$ (see Figure 8) we see a stronger correlation between temperatures and stratospheric H$_2$O profiles and a weakened role of CH$_4$.

In the modeled transit spectra in Figure 7 we clearly show the effect of reduced ozone, methane, and water for the high flaring scenarios when compared with the GCR reference case. All water and methane absorption features are reduced for the flaring case with $f_{\text{NOx}} = 0.0$, and even more suppressed for the $f_{\text{HOx}} = 2.0$ case (light-blue line). Because NOx and HOx from HEPs can form HNO$_3$ via the reaction NO$_2$+OH+M → HNO$_3$+M, this leads to the absorption features seen in Figure 7. We confirm the HNO$_3$ absorption around 11 μm to be an indicator of an N$_2$–O$_2$ atmosphere exposed to a high flaring stellar environment, as proposed by Tabataba-Vakili et al. (2016). The second absorption feature of nitric acid around 17 μm is only visible for the case of high HOx production from cosmic-ray-induced ion pairs. Hence, the measurement of this absorption band may be a hint of these values of HOx production per ion pair. Rauer et al. (2011) and Hedelt et al. (2013) have already analyzed the telescope time needed with a configuration based on JWST to identify various spectral features. With the S/N derived after Hedelt et al. (2013) we estimate that ~35 transits of a theoretical planet around AD...
LEO (distance to observer 4.9 pc) would be needed to identify the 11 μm HNO₃ band with a spectral resolution \( R = 100 \). The second HNO₃ feature around 17 μm might require already a few hundred transits compared with an estimated three to four transits with NIRSpec (in the \( R = 100 \) mode) on board JWST for the 4.2 μm CO₂ band. The third HNO₃ absorption feature around 21 μm might be hard to detect at all, as it already lies in the far-infrared where the H₂O continuum dominates.

### 5. Conclusions

We have performed atmospheric simulations of virtual Earth-like planets around the flaming M-star AD LEO with our cloud-free 1D climate-chemistry model and have compared the influence of flaring strength with the uncertainty ranges of chemical NOₓ–HOₓ production efficiencies.

New chemical insights found in this work are:

1. NOₓ–HOₓ: The chemical production efficiencies \( f_{NOx} \) and \( f_{HOx} \) can significantly influence biosignature chemistry and abundance in our model, as well as stratospheric temperatures, and are therefore potentially important for Earth-like planets around M-dwarf stars like AD LEO. In the Earth’s atmosphere, on the other hand, the influx of SEPs has a much stronger effect than \( f_{NOx} \) and \( f_{HOx} \), which makes the empirical determination of the latter challenging.

2. HNO₃: Spectroscopic transit measurements of exoplanets may be able to help constrain their stellar environments by looking at, e.g., HNO₃ features above 10 μm together with infrared O₃, H₂O, and CH₄ absorption bands. Especially the measurement of the HNO₃ features at 17 and 21 μm would hint toward high \( f_{HOx} \) production.

3. Cl: We introduce and discuss a change of the major CH₄ sink in the stratosphere from OH (lower stratosphere) to Cl (upper stratosphere). This may also become important for worlds with, e.g., high volcanic chlorine emissions.

4. O₃: We show that on Earth the UVB radiation from the Sun (G-star) is sufficient to limit global tropospheric smog O₃ abundance even in hypothetical high flaring Sun scenarios, while we confirm lower atmospheric build-up of O₃ for Earth-like planets around active M-stars like AD LEO, as has been modeled in multiple studies, e.g., Segura et al. (2005), Grenfell et al. (2012), Tabataba-Vakili et al. (2016).

5. N₂O: Atmospheric N₂O abundance runs into “saturation” for flaring cases regardless of stellar spectrum, flaring strengths, or stratospheric O₃ levels. N₂O reactions, e.g., with O(¹D), in addition to diffusion processes within the atmosphere counteract the O³–UV–N₂O coupling (See Figure 9). Hence, destruction of N₂O by cosmic rays is ineffective in our model.

Additionally, in our model OH is the major sink for CH₄ in the lower- to mid-atmosphere and is directly produced by SEPs, but we find that around high flaring solar-like stars atmospheric O₃ abundance can significantly drop, which itself is a major source of tropospheric OH production (see Figure 9). This lack of OH from O₃ can outweigh OH production from SEPs, subsequently causing unexpectedly high CH₄ abundance (see Figures 3 and 9). Furthermore, in the absence of other sources HNO₃ can become the main OH source throughout our entire model atmosphere for high flaring host star cases. Further work on this is needed to see for which range of planetary atmospheres HNO₃ may become important.

We would like to emphasize once more that NOₓ and HOₓ produced by cosmic rays can become important when studying Earth-like atmospheres around active M-stars.

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