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Neptune’s carbon monoxide profile and phosphine upper limits from Herschel/SPIRE*: Implications for interior structure and formation

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Abstract

On Neptune, carbon monoxide and phosphine are disequilibrium species, and their abundance profiles can provide insights into interior processes and the external space environment. Here we use Herschel/SPIRE (Spectral and Photometric Imaging REceiver) observations from 14.9–51.5 cm^{−1} to obtain abundances from multiple CO and PH₃ spectral features. For CO, we find that nine CO bands can be simultaneously fitted using a step profile with a 0.22 ppm tropospheric abundance, a 1.03 ppm stratospheric abundance, and a step transition pressure of 0.11 bar near the tropopause. This is in broad agreement with previous studies. However, we also find that the CO spectral features could be fitted, to well within measurement errors, with a profile that contains no tropospheric CO for pressure levels deeper than 0.5 bar,

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which is our preferred interpretation. This differs from previous studies that have assumed CO is well mixed throughout the troposphere, which would require an internal CO source to explain and a high O/H enrichment. Our interpretation removes the requirement for extreme interior O/H enrichment in thermochemical models and can finally reconcile D/H and CO measurements. If true, the lack of lower tropospheric CO would imply a decrease in Neptune’s interior water content, favouring a silicate-rich instead of an ice-rich interior. This would be consistent with a protoplanetary ice source with a similar D/H ratio to the current solar system comet population. The upper tropospheric and stratospheric CO at pressures less than 0.5 bar could then be entirely externally sourced from a giant impact as suggested by Lellouch et al. (2005). We also derive a $3\text{-}\sigma$ upper limit for PH_3 of 1.1 ppb at 0.4–0.8 bar. This is the most stringent upper limit to-date and is entirely consistent with predictions from a simple photochemical model.

Keywords: Neptune, Atmosphere, Interior, Composition, sub-millimetre

1. Introduction

Observations of bulk density, gravity, and moment of inertia show that Neptune and Uranus are significantly enriched in heavy elements compared to Jupiter, Saturn, and the solar composition (Hubbard et al., 1995; Podolak et al., 1995; Owen and Encrenaz, 2006; Irwin, 2009; Helled et al., 2011; Netelmann et al., 2013). Their interiors are expected to contain a significant proportion of ices due to their formation beyond the ice line in the solar nebula, where cold temperatures permitted formation and subsequent ingestion of icy planetesimals. However, the fraction of rock to ice and the nature of

the original planetesimals are currently not well understood and ice-rich and rock-rich interior models are both compatible with the available bulk density, gravity, and moment of inertia observations (Podolak et al., 1995; Helled et al., 2011; Nettelmann et al., 2013). The different formation scenarios and internal structures are consistent with subsets of available spectroscopic observations and important discrepancies remain, particularly when trying to reconcile D/H and O/H measurements (Feuchtgruber et al., 2013). Here we consider two of Neptune’s disequilibrium species, carbon monoxide (CO) and phosphine (PH₃), which have the potential to further constrain Neptune’s interior composition, formation, and external planetary environment.

CO has been observed on both Uranus (Encrenaz et al., 1996; Cavalié et al., 2014) and Neptune (Marten et al., 1993; Guilloteau et al., 1993; Naylor et al., 1994; Courtin et al., 1996; Lellouch et al., 2005; Marten et al., 2005; Hesman et al., 2007; Lellouch et al., 2010; Fletcher et al., 2010; Luszcz-Cook and de Pater, 2013). On Uranus CO has a stratospheric abundance of 7.1–9.0 ppb (Cavalié et al., 2014) and a 3- σ tropospheric upper limit of 2.1 ppb for pressures around 0.1–0.2 bar (Teanby and Irwin, 2013). On Neptune CO is much more abundant, with recent studies suggesting a step-type profile with 1–3 ppm in the stratosphere and up to 0.5 ppm in the troposphere (summarised in Table 1).

The CO vertical gradient can be used to determine whether its source is mixing from the deep interior or external supply from comets, micrometeorites, or interplanetary dust. However, there is some disagreement in the published abundances (Table 1). The most recent study by Luszcz-Cook and de Pater (2013) found 1–2 ppm in the stratosphere, 0–0.3 ppm in the

35 troposphere, and a transition pressure of ~ 0.1 bar (close to the tropopause).
 36 This is broadly consistent with Lellouch et al. (2005)’s stratospheric determi-
 37 nation of 1 ppm, but lower than their value of 0.5 ppm for the troposphere.
 38 Conversely, Hesman et al. (2007)’s tropospheric value is consistent with Lel-
 39 louch et al. (2005)’s, but has a stratospheric abundance 2–3 times higher.
 40 There is also considerable uncertainty on the pressure of the transition in
 41 the step profiles used in all three studies. The discrepancy of these results
 42 could be partly due to the difficulty of observing CO from ground-based tele-
 43 scopes. The wide CO line wings that probe the troposphere cannot usually
 44 be covered with a single observation due to instrument bandwidth limita-
 45 tions. Therefore, either only the central emission core is observed to obtain a
 46 stratospheric abundance, or multiple observations with different local oscil-
 47 lator tunings must be stitched together. Such observations require baseline
 48 matching, which introduces extra uncertainty as observations must be taken
 49 at different times with different sky and instrument background levels. There
 50 are also differences in the radiative transfer modelling approaches, in particu-
 51 lar the assumed temperature profile. Therefore, new space-based constraints
 52 would be extremely valuable.

53 CO is more thermodynamically stable at the higher temperatures of
 54 Neptune’s deep atmosphere ($\gtrsim 1000$ K, $\gtrsim 5000$ bar) and becomes less stable
 55 (and much less abundant) in comparison to the thermochemical-equilibrium
 56 favoured molecules methane and water in the colder outer region of Neptune’s
 57 hydrogen-rich atmosphere (Lodders and Fegley, 1994). However, CO de-
 58 struction reactions have a strong temperature dependence and rapid vertical
 59 mixing can advect CO to pressure levels where the CO destruction timescale

60 is longer than the mixing timescale, effectively quenching the CO destruction
 61 and allowing significant CO to mix into the troposphere and stratosphere.
 62 On Neptune this quenching is expected to occur at 2000–10000 bars and
 63 850–1100 K depending on the strength of vertical mixing (Luszcz-Cook and
 64 de Pater, 2013; Cavalié et al., 2017). Such rapid mixing should result in a
 65 uniform CO mixing ratio in the troposphere and stratosphere. For Neptune,
 66 plausible estimates of the temperature profile and vertical mixing suggest
 67 that O/H must be enriched by at least 280 times relative to solar compo-
 68 sition in order to reproduce the observed ~ 0.1 ppm CO in the troposphere
 69 (Luszcz-Cook and de Pater, 2013; Cavalié et al., 2017). However, such a large
 70 enrichment of O/H is not compatible with D/H measurements, which sug-
 71 gest more modest O/H enrichments of ~ 50 – 150 (Feuchtgruber et al., 2013)
 72 if Neptune’s internal water was sourced from protoplanetary ices with D/H
 73 comparable to present day comets. CO has not yet been detected in Uranus’
 74 troposphere (Teanby and Irwin, 2013), which could be due to less vigorous
 75 mixing.

76 The excess of CO in both Neptune and Uranus’ stratospheres compared to
 77 their tropospheres suggests a significant external CO source for both plan-
 78 ets (Lellouch et al., 2005; Cavalié et al., 2013). Estimates of the external
 79 flux required to explain observed H₂O and CO₂ abundances in Uranus and
 80 Neptune’s stratosphere were made by Feuchtgruber et al. (1997), suggesting
 81 H₂O external fluxes of 0.6 – 1.6×10^5 molecules cm⁻²s⁻¹ for Uranus and 1.2 –
 82 150×10^5 molecules cm⁻²s⁻¹ for Neptune. These inferred H₂O influx rates
 83 are broadly consistent with those expected from incoming interplanetary
 84 dust grains (Poppe, 2016). However, the predicted dust flux for Neptune

85 is roughly two orders of magnitude too small to explain the very large ob-
 86 served CO abundance in Neptune’s stratosphere, even if the oxygen from the
 87 dust grains were efficiently converted to CO (see Poppe, 2016; Moses and
 88 Poppe, 2017). The large concentration of CO in Neptune’s stratosphere led
 89 Lellouch et al. (2005) to suggest that the source of Neptune’s CO could be
 90 a large cometary impact that occurred ~ 200 years ago. This hypothesis is
 91 supported by the recent detection of CS by Moreno et al. (2017), an impact
 92 product that was also detected after the Shoemaker-Levy 9 impact on Jupiter
 93 (Moreno et al., 2003). Moreno et al. (2017) suggest a slightly larger 4 km
 94 diameter comet impacting ~ 1000 years ago.

95 Further constraints on Neptune’s atmosphere can be obtained by study-
 96 ing another disequilibrium species, phosphine (PH_3), which is only stable in
 97 the deep atmosphere, but could theoretically be transported to higher at-
 98 mospheric levels by rapid vertical mixing as on Jupiter and Saturn (Irwin
 99 et al., 2004; Fletcher et al., 2009). There is currently considerable uncer-
 100 tainty about Neptune’s phosphorous enrichment, but a P/H enrichment of
 101 50 times solar, similar to that inferred for C/H from methane measurements
 102 (Baines et al., 1995), is considered reasonable. However, observing PH_3 is
 103 challenging as it condenses in Neptune’s cold troposphere for pressures less
 104 than ~ 1 bar. Also, PH_3 is photodissociated by solar UV photons in the upper
 105 troposphere of giant planets (Kaye and Strobel, 1984; Moses, 2000), leading
 106 to additional depletion in the upper troposphere. This should result in sig-
 107 nificant PH_3 abundance only for pressures greater than ~ 1 – 2 bar, producing
 108 spectral features that are wide due to pressure broadening and with negligi-
 109 ble central emission core due to a lack of significant stratospheric abundance.

110 Nevertheless, an attempt was made to observe the 267 GHz (8.91 cm^{-1}) PH_3
 111 feature by Encrenaz et al. (1996) who determined that a 2 ppm deep PH_3
 112 abundance ($\sim 3\times$ solar P/H) coupled with super-saturation by a factor of 100
 113 above the condensation level was inconsistent with observations from the
 114 Caltech Submillimeter Observatory. More recently Moreno et al. (2009) de-
 115 termined a more stringent upper limit of 0.1 times the solar P/H value using
 116 the same PH_3 feature observed with the IRAM 30 m telescope, corresponding
 117 to an upper troposphere abundance upper limit of ~ 60 ppb (assuming a solar
 118 abundance of $\text{P/H} = 2.81 \times 10^{-7}$ from Lodders (2010)). Unfortunately, these
 119 upper limits are not sufficient to significantly inform photochemical models.

120 Here we use Herschel/SPIRE data to further constrain Neptune’s CO and
 121 PH_3 profiles. SPIRE is ideally suited to studying these gases as it covers a
 122 wide spectral range containing multiple CO and PH_3 features. This allows
 123 the line wings to be measured in a single measurement from a space-based
 124 platform with no atmospheric interference. This will permit the most sensi-
 125 tive search of PH_3 to date, more robust constraints on Neptune’s CO profile,
 126 and insights into Neptune’s interior and formation.

127 **2. Observations**

128 Observations were taken with the SPIRE instrument (Griffin et al., 2010;
 129 Swinyard et al., 2010) on board the Herschel Space Observatory (Pilbratt
 130 et al., 2010). SPIRE is a Fourier transform spectrometer comprising a
 131 long-wave spectrometer (SLW) covering wavenumbers $14.9\text{--}33.0 \text{ cm}^{-1}$ (671--
 132 $303 \mu\text{m}$) and a short-wave spectrometer (SSW) covering $31.9\text{--}51.5 \text{ cm}^{-1}$ (313--
 133 $194 \mu\text{m}$). The SPIRE spectrometers have hexagonal arrays of circular pixels;

134 37 pixels for the SLW and 19 pixels for the SSW. The unapodised spec-
 135 tral resolution can be set to low resolution (0.83 cm^{-1}), medium resolution
 136 (0.24 cm^{-1}), and high resolution (0.04 cm^{-1}). Herschel’s 3.5 m diameter pri-
 137 mary mirror combined with the pixel array footprints results in pixel beams
 138 with a field-of-view of $17\text{--}42''$, which is large compared to Neptune’s $\sim 2.3''$
 139 projected diameter, so observations are disc-averaged.

140 Herschel operated from 2009 until 2013, when it ran out of coolant, and
 141 all data are now archived. Uranus was used as the primary flux calibrator
 142 for the SPIRE spectrometer (Swinyard et al., 2014), but Neptune was also
 143 regularly observed for cross-calibration with the SPIRE photometer observa-
 144 tions (Swinyard et al., 2014; Hopwood et al., 2015). The pipeline radiance
 145 calibration used a Uranus reference spectrum combined with darks taken
 146 on a relatively empty area of sky, which were used to remove the instru-
 147 ment self-emission and characterise the instrument (Swinyard et al., 2010,
 148 2014; Hopwood et al., 2015). We queried the Herschel Science Archive for all
 149 science and calibration observations of Neptune taken with SPIRE in high
 150 resolution spectrometer mode so that the CO features could be resolved. The
 151 Level 2 unapodised calibrated radiances were extracted and convolved with
 152 a Hamming function to give an apodised spectral resolution of 0.07373 cm^{-1}
 153 (full-width half-maximum) and a sample spacing of 0.01 cm^{-1} . The CO ab-
 154 sorption features had widths of $\sim 0.5 \text{ cm}^{-1}$ and the widths of the central
 155 emission cores were limited by SPIRE’s spectral resolution. The Neptune-
 156 centred pixel from each observation was extracted to give a disc-average
 157 spectrum and associated pipeline uncertainties. After quality control of the
 158 observations to reject spectra with excessive noise or anomalously high/low

159 radiances, 17 Neptune observations remained with integration times from
 160 823–13762 s. Observations are summarised in Table 2 and Figure 1a and b.
 161 Total integration time on Neptune was 32687 s (9 hrs 4 mins 47 s), with all
 162 observations taking place during 2009 and 2010.

163 Prior to further analysis, the 17 individual spectra were combined into
 164 a single high signal-to-noise disc-average Neptune spectrum. To account for
 165 distance variations and slight calibration differences between observations the
 166 weighted average continuum radiances at 20.5–21.5 cm^{-1} and 39.5–40.5 cm^{-1}
 167 were calculated and individual spectra were rescaled to match the overall av-
 168 erage. This rescaling was required to allow representative variances on the
 169 combined spectrum to be calculated, but did not affect the overall mean ra-
 170 diance. All 17 observations were then combined into an average spectrum
 171 using the error weighted mean (Bevington and Robinson, 1992). To deter-
 172 mine the uncertainties on the combined spectrum we calculated both the
 173 error-weighted variance of the 17 spectra and the theoretical error weighed
 174 variance based on the pipeline uncertainties of each spectrum; whichever was
 175 the largest was used for the uncertainty. Overall uncertainties (standard er-
 176 ror) per spectral element were ~ 0.2 Jy for the SLW and ~ 0.3 Jy for the SSW.
 177 The combined average SLW and SSW spectra are shown in Figure 1c and d.
 178 CO absorption and emission features are clearly visible. However, the spectra
 179 still contain slight continuum ripples as noted in previous studies (Teanby
 180 and Irwin, 2013; Teanby et al., 2013). Removal of these ripples required
 181 comparison to a synthetic spectrum and is discussed in the next section.

182 3. Spectral modelling

183 To fit the observed SPIRE spectrum and retrieve the composition of CO
184 and PH₃ we used the NEMESIS radiative transfer code (Irwin et al., 2008),
185 which we have previously used to analyse SPIRE spectra for Uranus (Teanby
186 and Irwin, 2013) and Titan (Teanby et al., 2013), in addition to extensive
187 use for analysis of Neptune’s near-IR spectra (Irwin et al., 2011, 2014, 2016).

188 Our Neptune reference atmosphere had a nominal temperature profile
189 based on Voyager 2 radio occultation analysis by Lindal (1992) for pressures
190 greater than 15 mbar, AKARI spectroscopic analysis by Fletcher et al. (2010)
191 for pressures less than 10 mbar, and a linear interpolation (in log pressure)
192 in between. Temperature was gridded onto 71 levels between 0.6 μ bar and
193 6 bar on a regular logarithmic grid. There is some uncertainty regarding
194 Neptune’s tropospheric temperature structure, with differences up to 5 K
195 reported in the literature (for example, see discussion in Hesman et al., 2007;
196 Fletcher et al., 2010; Luszcz-Cook and de Pater, 2013). Therefore, we also
197 consider “Hot” and “Cold” profiles, which differ from the nominal profile
198 by ± 5 K (Figure 2). For the baseline atmospheric composition we assumed
199 a He/H₂ ratio of 0.15 (by volume) and a volume mixing ratio (VMR) of
200 0.003 for N₂ (Conrath et al., 1993). The CH₄ volume mixing ratio was set
201 to a deep value of 0.02, followed the saturation pressure vapour curve in the
202 upper troposphere, and had an abundance of 1.15×10^{-3} in the stratosphere
203 (Lellouch et al., 2015). There is some uncertainty on Neptune’s deep CH₄
204 abundance (see discussion in Irwin et al., 2014), but the effect on the SPIRE
205 spectrum is minimal. HCN only has minor spectral features in this range, but
206 we include the abundance profile of Marten et al. (2005) for completeness.

207 Spectroscopic parameters were the same as those used in Teanby and Irwin
208 (2013).

209 Synthetic spectra were generated using the correlated- k approximation
210 for computational efficiency (Goody and Yung, 1989; Lacis and Oinas, 1991;
211 Irwin et al., 2008). The k -tables included the Hamming instrument function
212 with a FWHM of 0.07373 cm^{-1} . To simulate the disc-averaged spectrum we
213 used the field-of-view averaging technique detailed in Teanby et al. (2013)
214 with 33 field-of-view points; 20 on Neptune’s disc and 13 covering the limb.
215 This accounted for limb brightening and limb darkening effects and was suffi-
216 cient to reduce the disc-averaged systematic modelling errors, due to emission
217 angle variation across Neptune’s disc, to at least five times below the level
218 of the observation uncertainties.

219 Observed spectra were corrected for minor continuum ripples by compar-
220 ison with synthetic spectra generated using the reference atmosphere. First,
221 synthetic spectra were created for an atmosphere containing no CO or PH₃.
222 Second, synthetic spectra were created for an atmosphere with the nominal
223 CO profile from Luszcz-Cook and de Pater (2013) and a PH₃ profile with a
224 deep abundance of 1 ppb with the saturation vapour pressure law applied.
225 Third, the difference between spectra with and without CO/PH₃ was used
226 to create a continuum mask where the difference was less than 0.05 Jy, at
227 least a factor of four below the observational uncertainties. Fourth, the mask
228 was applied to the observations to remove spectral regions surrounding the
229 CO and PH₃ line positions, leaving only the continuum points. Fifth, the
230 ratio between masked observation and synthetic was calculated and a smooth
231 cubic b-spline curve fitted using a knot spacing of 3 cm^{-1} for the SLW and

232 1.5 cm^{-1} for the SSW (Teanby, 2007). These knot spacings were large enough
 233 to only remove large scale ripples and did not affect the spectral features.
 234 The resulting correction factor f_{corr} is shown in Figure 1e and f and sug-
 235 gests continuum ripples of order $\pm 1\%$. Finally, the fitted smooth correction
 236 factor curve was applied to the observations to give the corrected SLW and
 237 SSW spectra shown in Figure 1g and h. This procedure was repeated for
 238 the nominal, hot, and cold temperature profiles. Note that a CO feature at
 239 15.38 cm^{-1} could not be analysed as it was at the low wavenumber edge of
 240 the SLW, so the surrounding continuum level could not be reliably corrected.

241 To determine the information content of our observed spectra we calcu-
 242 lated the contribution functions, defined as the change in irradiance as a
 243 function of gas abundance at each pressure level. The contribution functions
 244 for each of the CO bands are shown in Figure 3 assuming the SPIRE spec-
 245 tral resolution, the nominal temperature profile, and a 0.1 ppm uniform CO
 246 profile. In addition to the SPIRE CO bands, we also calculated the contribu-
 247 tion functions for the lower frequency CO (1–0), (2–1), and (3–2) transitions
 248 analysed in previous studies. Therefore, for this calculation the temperature
 249 profile was extended to 60 bar using the dry adiabatic lapse profile rate from
 250 Luszcz-Cook and de Pater (2013) so that contributions from the troposphere
 251 for the lowest frequency CO lines were fully determined. Note that con-
 252 tribution functions for the CO (1–0), (2–1), and (3–2) transitions are also
 253 calculated at the SPIRE spectral resolution, so are representative of the line
 254 wings only, not the central emission cores, which can sound to much lower
 255 pressure at high spectral resolution.

256 Figure 3 shows that there are two main pressure ranges where the SPIRE

257 spectra have information on CO abundance: ~ 1.0 – 0.1 bar from the wide
 258 tropospheric absorption wings of the CO lines, which are most prominent for
 259 the SLW observations; and ~ 0.001 – 0.01 bar from the narrow stratospheric
 260 emission cores of the CO lines, which are most prominent in the SSW ob-
 261 servations. The difference between SLW and SSW CO features is caused by
 262 increases in CO line strength and overall atmospheric opacity with increas-
 263 ing wavenumber across the SPIRE range. There is little or no information
 264 in the 0.01 – 0.1 bar region, which explains the large uncertainty in previ-
 265 ous determinations of the transition pressure in step-type CO profiles (see
 266 e.g. Luszcz-Cook and de Pater, 2013, and Table 1). The SPIRE data are
 267 not sensitive to the deep abundance (pressures greater than 1.0 bar), but
 268 have excellent coverage of the upper troposphere and stratosphere. The low-
 269 est frequency bands, including the CO (1–0), (2–1), and (3–2) transitions
 270 analysed in previous studies (Table 1), are sensitive to slightly lower deeper
 271 levels than our data. Given the limited bandwidth of previous observations
 272 (e.g. Luszcz-Cook and de Pater, 2013) Figure 3 shows the maximum pressure
 273 probed is ~ 3 bar for the CO (1–0) transition, assuming a 0.1 ppm uniform
 274 CO abundance.

275 The PH_3 contribution functions are shown in Figure 4 assuming a nom-
 276 inal deep abundance of 1 ppb and an abundance following the saturation
 277 vapour pressure curve in the troposphere, with a maximum stratospheric
 278 abundance set to that at the tropopause cold trap. Saturation vapour pres-
 279 sure temperature dependence was based on a fit to the low temperature
 280 vapour pressures in Lide (1995), giving the saturation vapour pressure in
 281 bars $P_{\text{SVP}}(T) = \exp(a + b/T + cT)$, where $a = 11.4600$, $b = -1974.44$ K, and

282 $c = -0.00435846 \text{ K}^{-1}$. The pressure level where PH_3 condenses is a strong
 283 function of temperature, anywhere from 0.1–1 bar, which gives very different
 284 contribution functions for the nominal, hot, and cold temperature profiles.
 285 However, there is very limited information for pressures greater than 1 bar
 286 in these data. There are four PH_3 spectral features covered by SPIRE (cen-
 287 tred on 17.81, 26.70, 35.59, and 44.46 cm^{-1}), but the features at 17.81 cm^{-1}
 288 (SLW) and 44.46 cm^{-1} (SSW) are the most favourable for a detection as
 289 they are well separated from the CO features. The optimal band for search-
 290 ing for PH_3 depends on the temperature profile and abundance profile, with
 291 the SLW being optimal for the cold and nominal profiles, and the SSW being
 292 optimal for the hot profile.

293 Spectra were fitted using NEMESIS’ iterative non-linear retrieval scheme
 294 (Irwin et al., 2008), which adjusts the composition profiles to minimise the
 295 misfit between modelled spectrum and observation. Simple parameterised
 296 profiles were used for both CO and PH_3 , so it was not necessary to impose
 297 apriori constraints on the retrieval scheme.

298 For fitting the CO spectral features we used three profile types: (1) a
 299 three parameter simple step profile, defined by a uniform deep abundance
 300 v_1 , a uniform stratospheric abundance v_2 , and a transition pressure p_1 ; (2)
 301 a four parameter gradient profile, defined by a uniform deep abundance v_1 ,
 302 a uniform stratospheric abundance v_2 , and two pressures p_1 and p_2 , which
 303 defined a transitional linear gradient region (in log pressure-abundance) from
 304 v_1 to v_2 ; and (3) a four parameter external gradient profile with zero deep
 305 abundance for pressures greater than p_1 , a linear transition region (in log
 306 pressure-abundance) defined by two pressure-abundance pairs (p_1, v_1) and

307 (p_2, v_2) , and uniform abundance v_2 at pressures less than p_2 . The step profile
 308 (1) has been used extensively in the literature to represent a combination
 309 of internal and external sources. The gradient profile (2) expands on the
 310 step profile slightly by allowing a finite mixing region. The external gradient
 311 profile (3) represents the case where there is no significant internal CO source
 312 and all tropospheric CO is mixed from above.

313 For PH_3 , we used a single parameter profile based on a uniform deep
 314 abundance modified by the saturation vapour pressure and with the strato-
 315 spheric abundance set to that at the troposphere cold trap.

316 4. Results

317 All nine CO spectral features were fitted simultaneously for each of the
 318 three CO profile types and assuming a nominal, hot, or cold temperature
 319 profile. Table 3 summarises the fit parameters for each case. The quality of
 320 each fit was assessed using the χ^2 statistic:

$$\chi^2 = \sum_{i=1}^N \left[\frac{I_{\text{obs}}(\nu_i) - I_{\text{fit}}(\nu_i)}{\sigma(\nu_i)} \right]^2 \quad (1)$$

321 where ν_i is the wavenumber, $I_{\text{obs}}(\nu_i)$ is the measured spectral irradiance,
 322 $I_{\text{fit}}(\nu_i)$ is the best fitting synthetic spectrum, $\sigma(\nu_i)$ is the observational error,
 323 and N is the number of points in the spectrum. The reduced χ^2 defined by
 324 χ^2/N should be ~ 1 if the synthetic spectrum fits the data within error.

325 The nominal temperature profile combined with the step CO profile had
 326 the lowest χ^2/N (0.63), which we consider our best fitting model. Figure 5
 327 shows the best fit to the nine CO features covered by SPIRE, assuming the
 328 nominal temperature profile and using the step profile with deep abundance

329 of 0.22 ppm, a stratospheric abundance of 1.03 ppm and a transition pressure
 330 of 0.11 bar. The reduced χ^2 is less than 1, suggesting the data are well fitted
 331 by this profile. In fact, the χ^2/N only exceeds 1 for the hot external gradient
 332 profile, but for all other cases the fits can be considered adequate. While
 333 the nominal temperature step profile technically provides the best fit to the
 334 data, it cannot be statistically distinguished from the other temperature / CO
 335 profile cases. Therefore, a wide range of profiles can fit these data, including
 336 those with no internal CO source. The fitted profiles are shown in Figure 6a
 337 and can all be considered plausible. The range of abundances obtained were
 338 0–0.36 ppm for the deep volume mixing ratio and 0.80–1.55 ppm for the
 339 stratospheric volume mixing ratio. The transition pressure range is not well
 340 determined by these data, but falls between 0.11–0.75 bar.

341 None of the four phosphine spectral features covered by SPIRE were
 342 visible in the data. Therefore, we determined upper limits using a modified
 343 χ^2 , $\chi_r^2(v)$:

$$\chi_r^2(v) = \frac{\Delta\nu_{\text{obs}}}{\Delta\nu_{\text{res}}} \sum_{i=1}^N \left[\frac{I_{\text{obs}}(\nu_i) - I_{\text{fit}}(\nu_i, v)}{\sigma(\nu_i)} \right]^2 \quad (2)$$

344 where $\Delta\nu_{\text{obs}}$ is the observation wavenumber spacing (0.01 cm^{-1}), $\Delta\nu_{\text{res}}$ is the
 345 observation spectral resolution (0.07373 cm^{-1}), and v is the deep PH_3 volume
 346 mixing ratio. The factor $\Delta\nu_{\text{obs}}/\Delta\nu_{\text{res}}$ accounts for the spectral oversampling.
 347 The PH_3 profile is defined by one parameter so the $3\text{-}\sigma$ upper limit is defined
 348 as the abundance which increases χ_r^2 by +9 (Press et al., 1992).

349 Figure 7 shows the variation of $\Delta\chi_r^2 = \chi_r^2(v) - \chi_r^2(0)$ as a function of PH_3
 350 abundance for the nominal, hot, and cold temperature profiles, along with the
 351 observed spectra and $3\text{-}\sigma$ upper limit synthetics. The SLW 17.81 cm^{-1} and

SSW 44.46 cm^{-1} bands were considered independently and the best upper limits for each assumed temperature profile are summarised in Table 4. The PH_3 upper limit for the nominal temperature profile was 1.10 ppb. Figure 6b shows the upper limits and indicates the pressure range of the information content.

5. Discussion

5.1. CO profile

Our retrieved CO abundances are broadly consistent with previous results and agree with those presented by Luszcz-Cook and de Pater (2013) (Table 1). The step profile results provide the most direct comparison as this profile was also used in the previous studies (Lellouch et al., 2005; Hesman et al., 2007; Lellouch et al., 2010; Luszcz-Cook and de Pater, 2013). Our preferred deep abundance of 0.21–0.24 is most consistent with Luszcz-Cook and de Pater (2013) and Hesman et al. (2007), whereas our stratospheric abundance of 0.80–1.41 is most consistent with Luszcz-Cook and de Pater (2013) and Lellouch et al. (2005). The advantage of our CO profiles over previous studies is that the SPIRE data cover a much larger spectral range, allowing the wide CO line wings and narrow emission cores to be measured at the same time. We also fit nine CO bands simultaneously, providing an extra consistency check compared to previous studies, which fitted between one and three bands (Table 1). However, the SPIRE observations are at relatively low spectral resolution compared to previous microwave studies, so cannot fully resolve the emission cores, resulting in reduced sensitivity

375 at very low pressures (<0.1 mbar). Our observations are also at higher fre-
376 quency compared to previous studies and do not sound below 1 bar.

377 One key feature of the SPIRE observations is they do not require sig-
378 nificant CO for pressures greater than 0.5 bar, and CO is only required in
379 the upper troposphere (0.1–0.5 bar) to adequately fit the data. This was
380 also apparent in some of the solutions found by Luszcz-Cook and de Pater
381 (2013), which included the J=1-0 line at 115.271 GHz, which has contribu-
382 tion functions that extend slightly deeper than our data (to ~ 3 bar assuming
383 a uniform CO profile (Figure 3)).

384 Therefore, by combining our results with those of Luszcz-Cook and de Pa-
385 ter (2013) we infer that while some CO is required in the upper troposphere
386 (0.1–0.5 bar) to fit the observations, it is not a requirement to have signifi-
387 cant amounts at deeper pressures. This has important implications for the
388 formation and composition of Neptune’s deep atmosphere and could resolve
389 some of the apparent discrepancies between CO and D/H measurements.

390 5.2. Neptune’s formation and internal structure

391 D/H in Neptune’s atmosphere has been measured to be $4.1 \pm 0.4 \times 10^{-4}$
392 from Herschel/PACS observations (Feuchtgruber et al., 2013). When this is
393 combined with water-rich interior models fitted to mass, moment of inertia,
394 and gravitational coefficients from the Voyager 2 flyby (Hubbard et al., 1995;
395 Podolak et al., 1995; Helled et al., 2011; Nettelmann et al., 2013), this value
396 of D/H suggests the icy planetesimals that formed Neptune had D/H ratios
397 of $5.1\text{--}7.7 \times 10^{-5}$. This is $\sim 2\text{--}3$ times less enriched than any known source
398 material in the present day solar system, with comets having a D/H ratio of
399 $\sim 1.5\text{--}3.0 \times 10^{-4}$ (Hartogh et al., 2011).

400 One potential solution proposed by Feuchtgruber et al. (2013) is to in-
 401 crease the silicate content of the pre-Neptune planetesimals to 68–86% rock
 402 an 14–32% ice, i.e. similar to the estimated bulk rock fraction of Pluto (Si-
 403 monelli and Reynolds, 1989). This would give Neptune a more rock-rich
 404 interior compared to more conventional water-rich internal models (Hubbard
 405 et al., 1995) and would allow water to be sourced from ices with D/H in the
 406 range of current comets ($1.5\text{--}3.0\times 10^{-4}$). The reduced ice content then puts
 407 the O/H enrichment contribution due to Neptune’s water ice content to be
 408 50–150 times solar (Feuchtgruber et al., 2013). This solution is appealing as
 409 the resulting inferred rock content is also consistent with predictions from
 410 the Solar Composition Icy Planetesimals (SCIPs) model of planet forma-
 411 tion (Owen and Encrenaz, 2006) and simple formation models using either
 412 comet-like or clathrate-hydrate planetesimals (Ali-Dib and Lakhani, 2018).
 413 The inferred O/H enrichment is also comparable with C/H enrichment, which
 414 is estimated at ~ 50 times solar based on methane measurements by Baines
 415 et al. (1995).

416 However, a problem arises when comparing this potential formation and
 417 interior model with thermochemical schemes for CO, which require highly
 418 enriched O/H ratios of 280–650 times solar to allow sufficient mixing of CO
 419 into the troposphere to explain the previously derived ~ 0.1 ppm abundances
 420 (Lodders and Fegley, 1994; Luszcz-Cook and de Pater, 2013; Cavalié et al.,
 421 2017). For example, Cavalié et al. (2017) used a 1-D thermochemical kinetics
 422 and transport model to predict the CO mixing ratio profile on Neptune for
 423 different assumptions about the deep O/H abundance. They found that a
 424 deep atmospheric O/H ratio of ~ 540 times the solar ratio was required to

425 explain a tropospheric CO mixing ratio of 0.2 ppm, if they assumed the fast
 426 $\text{CO} \rightarrow \text{CH}_4$ chemical conversion scheme described in Venot et al. (2012).
 427 However, as is discussed by Visscher et al. (2010), Moses et al. (2011), and
 428 Moses (2014), the adoption of a very large rate coefficient for the reaction H
 429 $+ \text{CH}_3\text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O}$ in the Venot et al. (2012) scheme likely leads to
 430 an overestimate in the required deep O/H abundance on the giant planets.
 431 Using the Moses et al. (2011) rate coefficient for this reaction, Cavalié et al.
 432 (2017) derive a deep O/H ratio of ~ 280 for Neptune in order to produce an
 433 upper tropospheric CO mixing ratio of 0.2 ppm. This O/H value is still too
 434 large to be compatible with the D/H ratio, as discussed above.

435 One potential solution to reconcile the CO and D/H measurements is to
 436 form Neptune (and Uranus) on the CO ice line (Ali-Dib et al., 2014). In this
 437 model CO pebbles are concentrated near the ice line due a combination of
 438 rapid outward diffusion of CO gas and slow inward migration of pebbles due
 439 to gas drag. If Neptune forms close to this ice line then the pre-Neptune
 440 planetesimals are largely composed of CO instead of H_2O , resulting in the
 441 bulk of Neptune’s water originating from transformation of CO into H_2O
 442 in the planets interior. This would then be compatible with a higher more
 443 comet-like D/H ratio for the water-rich planetesimals contributing to Nep-
 444 tune’s formation.

445 We propose an alternative and perhaps simpler solution – that there is in
 446 fact no significant tropospheric CO for pressures greater than ~ 0.5 bar – and
 447 that the majority of Neptune’s observable CO is externally sourced. This hy-
 448 pothesis would be consistent with our observations and those of Luszcz-Cook
 449 and de Pater (2013) and relaxes the requirement for extreme O/H enrich-

450 ment in the deep interior. A requirement of this scenario is that the eddy
 451 mixing coefficient K in the upper troposphere is reduced so that sufficient
 452 CO from a comet impact can be maintained in the 0.1–0.5 bar pressure range
 453 to fit the observations. The current estimate of $K=10^8 \text{ cm}^2\text{s}^{-1}$ in the deep
 454 troposphere is based on mixing length theory and internal heat flux (Moses,
 455 1992; Moses et al., 1992) and in the absence of other constraints is generally
 456 applied to the whole troposphere. However, this heat flux is effectively emit-
 457 ted from the radiative convective boundary, which is likely to be somewhat
 458 below the tropopause. Comparing Neptune’s observed brightness tempera-
 459 ture of 60 K near the $\sim 100 \mu\text{m}$ peak of its infrared emission (Burgdorf et al.,
 460 2003) to the temperature profiles in Figure 2 suggests a pressure level of
 461 ~ 0.5 bar for this emission level. The lapse rate is also somewhat reduced in
 462 the upper troposphere region, suggesting a more stable atmosphere close to
 463 the tropopause than deeper in the atmosphere. Therefore, a reduced K in
 464 the 0.1–0.5 bar range is plausible, and is also in line with requirements from
 465 recent photochemical modelling (Moses et al., 2018). In this case the external
 466 CO source would also still be compatible with the giant comet impact pro-
 467 posed by (Lellouch et al., 2005) and supported by (Moreno et al., 2017). The
 468 silicate-rich Neptune suggested by Feuchtgruber et al. (2013) would then be
 469 more compatible with the available observations than a water-rich Neptune.

470 *5.3. Phosphorous chemistry*

471 Our PH_3 upper limits of 0.192–5.52 ppb for 0.1–1.2 bar are one to two
 472 orders of magnitude more stringent than previous determinations (Encrenaz
 473 et al., 1996; Moreno et al., 2009) and show that PH_3 can be considered
 474 negligible in the upper troposphere and stratosphere. If the tropospheric

475 PH₃ profile is determined entirely by condensation of a deep abundance then
 476 our upper limits are significantly sub-solar; corresponding to enrichments
 477 of 3.93×10^{-4} – 1.13×10^{-2} times the Lodders (2010) solar values (Table 4).
 478 This is at least three orders of magnitude below the expected ~ 50 times
 479 enrichment expected from methane measurements and formation models, so
 480 suggests other loss processes must be active.

481 To test whether the lack of PH₃ in this region of Neptune’s atmosphere
 482 has a photochemical origin, we developed a simple, global-average, one-
 483 dimensional model for tropospheric and stratospheric chemistry on Neptune
 484 that includes PH₃ photochemistry, using the Caltech/JPL KINETICS code
 485 (Allen et al., 1981; Yung et al., 1984). The model inputs are similar to those
 486 discussed by Moses and Poppe (2017), but we add nitrogen and phospho-
 487 rous species and reactions based on the Jupiter and Saturn studies described
 488 in Kaye and Strobel (1983b), Kaye and Strobel (1983a), Kaye and Strobel
 489 (1984), Visscher et al. (2009), Moses et al. (2010), and Fletcher et al. (2018).
 490 We assume that the PH₃ mixing ratio at the model lower boundary (8 bar)
 491 is either 2.0×10^{-5} or 4.6×10^{-5} ($\sim 30x$ or $\sim 70x$ solar, based on the protosolar
 492 abundances of Lodders et al. (2009)). The eddy diffusion coefficient profile
 493 adopted in the model is shown in Fig. 4 of Moses et al. (2018), and is based on
 494 the hydrocarbon photochemical modelling discussed in Moses et al. (2005).
 495 Although the eddy diffusion coefficients increase with increasing altitude in
 496 the stratosphere of Neptune, Moses et al. (2005, 2018) find that the eddy
 497 diffusion coefficient must be small (assumed $400 \text{ cm}^2\text{s}^{-1}$) in the upper tropo-
 498 sphere and/or lower stratosphere of Neptune in order for the large observed
 499 C₂H₆ abundance to be reproduced. This is consistent with the qualitative

radiative arguments given in Section 5.2. Our models include absorption of solar radiation by atmospheric gases and multiple Rayleigh scattering by gaseous H_2 , He, and CH_4 , but we do not consider aerosol extinction.

The results from this photochemical model indicate that PH_3 should be confined to pressures greater than ~ 1 bar on Neptune (Figure 6b), consistent with our derived PH_3 upper limits. Phosphine is photolysed by solar ultraviolet photons with wavelengths less than 230 nm. The main products are $\text{PH}_2 + \text{H}$. The resulting atomic H can also react with PH_3 to produce $\text{PH}_2 + \text{H}_2$, and two PH_2 radicals can combine to form P_2H_4 , which then condenses (Ferris and Benson, 1981; Kaye and Strobel, 1984). In this way, the PH_3 is relatively efficiently converted to diphosphine and other phosphorus-bearing aerosols in Neptune’s troposphere. Solar photons with wavelengths less than 230 nm do not penetrate past the $\sim 2\text{--}3$ bar level in Neptune’s troposphere, but multiple Rayleigh scattering allows significant photolysis of PH_3 in the $\sim 0.5\text{--}2.5$ bar region, limiting the vertical extent of PH_3 . The low eddy diffusion coefficient in this region prevents PH_3 from being transported up faster than it can be destroyed by photolysis. This result could change if the eddy diffusion coefficient in the upper troposphere were greater than we have assumed or if aerosols (not included in the model) shield the PH_3 from photolysis. Our strong upper limits on the PH_3 mixing ratio in the 0.5–1 bar region will allow for useful constraints on the strength of atmospheric mixing in the upper troposphere of Neptune using future models that include aerosol extinction.

523 6. Conclusion

524 We used all available Herschel/SPIRE observations to constrain Nep-
525 tune’s CO and PH₃ abundances. A simultaneous fit of all nine CO bands
526 was possible using conventional step profiles, gradient profiles, and profiles
527 with zero deep abundance for pressures greater than 0.5 bar. The fitting
528 of multiple CO bands simultaneously improved the robustness of our abun-
529 dance results. Our abundances ranged from 0.80–1.55 ppm in the strato-
530 sphere (<0.1 bar) and 0.21–0.36 in the upper troposphere (1.0–0.1 bar), in
531 broad agreement with previous studies.

532 Importantly, the Herschel/SPIRE data do not require tropospheric CO
533 to exist at pressure levels deeper than 0.5 bar. This is also true of previous
534 observations of longer wavelength CO lines by Luszcz-Cook and de Pater
535 (2013) that probe slightly deeper (~ 3 bar for the 115 GHz line depending on
536 profile assumptions). Therefore, both our observations and those previously
537 published are not very sensitive to the deep CO abundance, meaning that we
538 cannot confirm or deny the presence of CO for pressures deeper than 1 bar.
539 Caution must then be used in assuming that abundances measured in the
540 upper troposphere are representative of the deep interior.

541 We suggest that the ~ 0.1 – 0.2 ppm deep tropospheric abundances previ-
542 ously reported could in fact be a result of extrapolating an idealised profile
543 to pressures where the data do not constrain the CO abundance. If this is
544 the case then extreme O/H enrichments would no longer be required in ther-
545 mochemical interior models to explain a CO abundance throughout the tro-
546 posphere, which allows the CO abundance profile and D/H measurements to
547 be reconciled. This means that current solar system water reservoirs become

548 a plausible water source, especially if the rock content of Neptune’s interior
549 can be increased to dilute the high D/H ratio in these sources. The bulk of
550 Neptune’s stratospheric and tropospheric CO can then be considered entirely
551 externally sourced from a large cometary impact within the past few hundred
552 years. We propose that a rock-rich Neptune as proposed by Feuchtgruber
553 et al. (2013) is more compatible with the current geophysical/spectroscopic
554 observations and possible formation scenarios.

555 PH₃ upper limits are sensitive to the temperature profile assumptions,
556 but fall in the range 0.192–5.52 ppb for the 0.1–1.2 bar pressure range, with
557 a nominal value of 1.10 ppb. This corresponds to 3.93×10^{-4} – 1.13×10^{-2}
558 times the solar value, which requires loss processes other than condensation
559 to explain. This is most likely due to photochemistry and the derived upper
560 limits are consistent with our simple photochemical modelling, which predicts
561 negligible PH₃ in this pressure region.

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Study	Telescope	Freq.	Wavenumber	Uniform†	Step‡		
		(GHz)	(cm ⁻¹)	(ppm)	v_1 (ppm)	v_2 (ppm)	p_1 (bar)
Luszcz-Cook and de Pater (2013)	CARMA	115.271	3.845	-	0–0.3	0.93–1.9	0.0025–0.2
	CARMA	230.538	7.670	-	"	"	"
	CARMA	345.796	11.535	-	"	"	"
Lellouch et al. (2010)	Herschel/PACS	~1750	~60	-	~0.5	~1	~0.01
Hesman et al. (2007)	JCMT	345.796	11.535	-	0.6±0.4	2.2 ^{+0.6} _{-0.4}	0.006
Lellouch et al. (2005)	IRAM	230.538	7.670	-	0.5±0.1	1±0.2	0.02
Marten et al. (2005)	IRAM	230.538	7.670	1.0±0.2	-	-	-
	JCMT	345.796	11.535	"	-	-	-
	JCMT	461.040	15.379	"	-	-	-
Naylor et al. (1994)	JCMT	230.538	7.670	1.0±0.3	-	-	-
Guilloteau et al. (1993)	IRAM	115.271	3.845	0.6–1.5	-	-	-
Marten et al. (1993)	CSO	230.538	7.670	1.2±0.4	-	-	-
	JCMT	345.796	11.535	"	-	-	-
Rosenqvist et al. (1992)	IRAM	230.538	7.670	0.65±0.35	-	-	-

Table 1: Summary of previous microwave and far-IR CO studies. † Early studies used a profile with a uniform mixing ratio throughout the troposphere and stratosphere. ‡ Recent studies assume a step-type profile defined by a transition pressure p_1 , a high pressure uniform abundance v_1 , and a low pressure uniform abundance v_2 .

Obs. ID	Start Time (UT)	Integration Time (s)	RA ($^{\circ}$)	DEC ($^{\circ}$)	Dist. (AU)	Disc ($''$)
1342187090	2009-11-19 05:52:45.0	823.0	326.06	-14.06	30.07	2.27
1342187883	2009-12-09 00:26:43.0	823.0	326.34	-13.97	30.40	2.25
1342187884	2009-12-09 00:40:54.0	823.0	326.31	-13.98	30.40	2.25
1342187887	2009-12-09 01:23:18.0	876.0	326.32	-13.97	30.40	2.25
1342195348	2010-04-21 19:57:15.0	1145.0	330.47	-12.53	30.46	2.24
1342195771	2010-05-03 19:03:43.0	1145.0	330.68	-12.46	30.27	2.26
1342196617	2010-05-17 04:43:33.0	1145.0	330.83	-12.42	30.05	2.27
1342197362	2010-05-31 11:27:26.0	1145.0	330.90	-12.41	29.80	2.29
1342197363	2010-05-31 11:46:49.0	1145.0	330.88	-12.42	29.80	2.29
1342197364	2010-05-31 12:06:10.0	1145.0	330.89	-12.42	29.80	2.29
1342197365	2010-05-31 12:25:33.0	1145.0	330.90	-12.39	29.80	2.29
1342197366	2010-05-31 12:44:56.0	1145.0	330.87	-12.40	29.80	2.29
1342197367	2010-05-31 13:04:17.0	1145.0	330.88	-12.39	29.80	2.29
1342197368	2010-05-31 13:23:38.0	3597.0	330.89	-12.40	29.80	2.29
1342198429	2010-06-09 19:52:13.0	13762.0	330.87	-12.42	29.65	2.30
1342208385	2010-11-08 00:51:49.0	839.0	328.16	-13.40	29.82	2.29
1342210841	2010-12-05 15:26:40.0	839.0	328.39	-13.32	30.29	2.25
Total		32687.0				

Table 2: Summary of SPIRE observations extracted from the Herschel Science Archive (<http://archives.esac.esa.int/hsa/whsa/>). RA, right ascension; DEC, declination; Dist., distance between Neptune and Herschel; and Disc, projected diameter of Neptune on the sky.

Temperature profile	CO profile type	Pressure		VMR		χ^2/N
		p_1 (bar)	p_2 (bar)	v_1 (ppm)	v_2 (ppm)	
Cold	Step	0.14	—	0.21	0.80	0.69
Cold	Gradient	0.74	0.0009	0.23	0.91	0.74
Cold	External gradient	0.48	0.0018	0.35	0.93	0.79
Nominal	Step	0.11	—	0.22	1.03	0.63
Nominal	Gradient	0.75	0.0013	0.23	1.19	0.67
Nominal	External gradient	0.48	0.0035	0.36	1.01	0.89
Hot	Step	0.10	—	0.24	1.41	0.86
Hot	Gradient	0.54	0.0023	0.24	1.55	0.89
Hot	External gradient	0.47	0.0073	0.39	1.52	1.21

Table 3: Retrieved CO profile parameters assuming the nominal, hot, and cold temperature profiles in Figure 2. The external gradient profile has zero abundance for pressures greater than p_1 . χ^2/N is the reduced χ^2 misfit and should be ~ 1 for a model fitting the data to within error – all profiles except the hot external gradient profile provide adequate fits to the data. The nominal temperature profile with a step CO abundance profile (shown in bold) provides the best fit to the observations (Figure 5 and 6).

Temperature profile	Optimal spectrometer	PH ₃ band centre (cm ⁻¹)	Pressure sensitivity (bar)	3- σ UL (ppb)	3- σ UL (x solar P/H [†])
Cold	SLW	17.81	0.8–1.2	<5.52	<1.13×10 ⁻²
Nominal	SSW	44.46	0.4–0.8	<1.10	<2.25×10 ⁻³
Hot	SSW	44.46	0.1–0.7	<0.192	<3.93×10 ⁻⁴

Table 4: PH₃ 3- σ upper limits for the three temperature profiles. In each case the optimal spectrometer is the one giving the lowest upper limit. Pressure sensitivity is the full-width half-maximum of the contribution functions shown in Figure 4 and in the absence of photochemistry is determined by the saturation vapour pressure curve.

[†] Equivalent enrichment relative to solar P/H using the abundances from Lodders (2010), i.e. solar P/H=0.281×10⁻⁶, implying a solar composition volume mixing ratio PH₃/(H₂+He)=0.489×10⁻⁶ (assuming that He/H₂=0.15 and all phosphorous is the form of PH₃).

Figure 1: Neptune SPIRE SLW and SSW spectra. (a,b) Individual spectra from the 17 observations in Table 2. (c,d) Weighted mean spectra compared with synthetic baseline spectra (no CO or PH_3) for nominal, hot, and cold temperature profiles. (e,f) Ratio of synthetic spectra to observation in continuum regions for nominal temperature case. The smooth cubic b-spline curve is used to correct the observation for large scale continuum ripples. (g,h) Corrected spectrum for nominal temperature case and (i,j) standard error uncertainties. CO features are clearly visible in the data (labelled).

Figure 2: Neptune temperature profiles. The hot and cold profiles are ± 5 K from the nominal case, which is based on Lindal (1992) and Fletcher et al. (2010). Our analysis is performed using all three profiles to include the current uncertainty in Neptune’s temperature structure.

Figure 3: Contribution functions for CO microwave bands. Calculations assume the SPIRE spectral resolution of 0.07373 cm^{-1} , the nominal temperature profile in Figure 2, and 0.1 ppm uniform CO abundance throughout the atmosphere. The upper tropospheric CO abundance gives wide absorption (negative/blue) features that are most prominent at lower frequencies, whereas the stratospheric abundance gives a narrow emission peak (positive/red) that is most prominent at higher frequencies. (a–c) Lowest frequency CO bands studied previously (e.g. by Luszczyk-Cook and de Pater, 2013). (d–m) CO bands covered SPIRE, with * indicating the bands analysed here. (n) Total normalised contribution function summed over all analysed wavenumbers in (e–m) for 1 ppm CO (red) and 0.1 ppm CO (blue), appropriate for the stratosphere and troposphere respectively. Solid/dashed line indicates where these abundances are appropriate/not appropriate. Information content is restricted to the 0.001–0.01 and 0.1–1 bar pressure regions for SPIRE. The lower frequency lines (a–c) probe slightly deeper to ~ 3 bar, assuming a typical 5–10 GHz bandwidth (Luszczyk-Cook and de Pater, 2013). The transition pressure used to define the step profile in previous studies typically falls in the 0.01–0.1 bar region, where there is little sensitivity.

Figure 4: Phosphine contribution functions for the 17.81 cm^{-1} (a–d) and 44.46 cm^{-1} (e–h) features under different temperature profile assumptions. For the nominal and cold cases saturation limits stratospheric abundances to negligible amounts. For the hot case some PH_3 can enter the stratosphere giving a small emission feature. (d,h) Total normalised contribution function summed over all wavenumbers in each band. Information is limited to the upper troposphere (0.1–1.2 bar).

Figure 5: Fitted CO features using the nominal temperature profile and a step VMR profile (bold profile highlighted in Table 3, and plotted in Figure 6). All nine CO bands are well fitted. The other profiles in Table 3 provide comparable fit qualities.

Figure 6: Fitted CO VMR profiles and PH_3 upper limits. (a) CO profiles have 0.80–1.55 ppm in the stratosphere and 0.21–0.39 ppm in the upper troposphere. These data do not require significant deep CO abundance. (b) Phosphine upper limits are consistent with our simple photochemical model profiles, which predict significant PH_3 removal by photolysis for pressures less than ~ 2 bar. Upper limit profiles are limited by condensation, which occurs at pressures less than ~ 1 bar. Note that the hot profiles require more stratospheric CO due to the rescaling of the continuum, which increases the contrast of the emission peak (the opposite is true for the cold profile).

Figure 7: Phosphine upper limits. (a,d,g) variation of χ^2 as a function of deep phosphine abundance for the two spectral bands and all three temperature profiles. No significant PH₃ is detected and upper limits of 0.192–5.52 ppb are inferred. Observations and synthetics with zero PH₃ abundance, 3- σ PH₃ abundance, and an enhanced abundance to show the PH₃ feature shape more clearly are shown in (b,c) for the cold profile, (e,f) for the nominal profile, and (h,i) for the hot profile.