Next-generation Isoprene Measurements from Space: Quantifying Daily Variability at High Resolution

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Abstract

Isoprene is the dominant non-methane organic compound emitted to the atmosphere, where it drives ozone and aerosol production, modulates atmospheric oxidation, and interacts with the global nitrogen cycle. Isoprene emissions are highly variable and uncertain, as is the non-linear chemistry coupling isoprene and its primary sink, the hydroxyl radical (OH). Space-based isoprene measurements can help close the gap on these uncertainties, and when combined with concurrent formaldehyde data provide a new constraint on atmospheric oxidation regimes. Here we present a next-generation machine-learning isoprene retrieval for the Cross-track Infrared Sounder (CrIS) that provides improved sensitivity, lower noise, and thus higher space-time resolution than earlier approaches. The Retrieval of Organics with CrIS Radiances (ROCR) isoprene measurements compare well with previous space-based retrievals as well as with the first-ever ground-based isoprene column measurements, with 20-50% discrepancies that reflect differing sources of systematic uncertainty. An ensemble of sensitivity tests points to the spectral background and isoprene profile specification as the most relevant uncertainty sources in the ROCR framework. We apply the ROCR isoprene algorithm to the full CrIS record from 2012-2020, showing that it can resolve fine-scale spatial gradients at daily resolution over the world's isoprene hotspots. Results over North America and Amazonia highlight emergent connections between isoprene abundance and daily-to-interannual variations in temperature, nitrogen oxides, and drought stress.

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19 Key Points:

- We present a next-generation spaced-based isoprene retrieval with higher sensitivity and resolution than previous approaches
- Global, daily isoprene distributions are derived from 2012-2020 that compare well with
 the first ground-based isoprene column observations
- High-resolution results over isoprene hotspots highlight processes controlling isoprene abundance and its daily-to-interannual variability
- 26

27 Abstract

28 Isoprene is the dominant non-methane organic compound emitted to the atmosphere, where it 29 drives ozone and aerosol production, modulates atmospheric oxidation, and interacts with the global nitrogen cycle. Isoprene emissions are highly variable and uncertain, as is the non-linear 30 31 chemistry coupling isoprene and its primary sink, the hydroxyl radical (OH). Space-based 32 isoprene measurements can help close the gap on these uncertainties, and when combined with 33 concurrent formaldehyde data provide a new constraint on atmospheric oxidation regimes. Here we present a next-generation machine-learning isoprene retrieval for the Cross-track Infrared 34 35 Sounder (CrIS) that provides improved sensitivity, lower noise, and thus higher space-time 36 resolution than earlier approaches. The Retrieval of Organics with CrIS Radiances (ROCR) 37 isoprene measurements compare well with previous space-based retrievals as well as with the 38 first-ever ground-based isoprene column measurements, with 20-50% discrepancies that reflect 39 differing sources of systematic uncertainty. An ensemble of sensitivity tests points to the spectral 40 background and isoprene profile specification as the most relevant uncertainty sources in the ROCR framework. We apply the ROCR isoprene algorithm to the full CrIS record from 2012-41 2020, showing that it can resolve fine-scale spatial gradients at daily resolution over the world's 42 43 isoprene hotspots. Results over North America and Amazonia highlight emergent connections 44 between isoprene abundance and daily-to-interannual variations in temperature, nitrogen oxides, 45 and drought stress.

46 Plain Language Summary

47 Isoprene is a naturally occurring trace gas emitted primarily from the leaves of woody plants. Isoprene has important impacts on both air quality and climate; however, these impacts are 48 49 difficult to assess and predict given large uncertainties in its sources and atmospheric chemistry. 50 Space-based measurements can help to address these uncertainties. Here we present new satellite 51 measurements of isoprene from the Cross-track Infrared Sounder (CrIS), using a computationally 52 efficient machine-learning framework (Retrieval of Organics from CrIS Radiances; ROCR). 53 ROCR measurements provide improved sensitivity and richer spatiotemporal information on 54 atmospheric isoprene than was previously available. Results compare well to previous satellite-55 based approaches and to new ground-based observations. We apply the ROCR framework to 56 measure daily, global isoprene distributions from 2012-2020. Results over North America and

Amazonia highlight the processes controlling isoprene abundances and their variability overtime.

59 1 Introduction

60 Isoprene is the dominant non-methane volatile organic compound (VOC) emitted to the atmosphere (Guenther et al., 2012). Produced mainly in the leaves of woody plants, isoprene is 61 62 highly reactive and drives ozone and aerosol production (Lin et al., 2013; Paulot et al., 2012), modulates atmospheric oxidation (Bates and Jacob, 2019), and affects the global nitrogen cycle 63 (Mao et al., 2013; Paulot et al., 2013). Accurate flux estimates are critical for assessing and 64 predicting these impacts; however, bottom-up isoprene inventories are highly uncertain as they i) 65 rely on emission factors extrapolated from limited point measurements and ii) are sensitive to 66 67 model assumptions for land cover, meteorology, and plant canopy structure (Arneth et al., 2011; 68 Messina et al., 2016; Ganzeveld et al., 2002). Particular uncertainties have been identified in the world's isoprene hotspots such as Amazonia, where studies show that isoprene exhibits much 69 70 stronger seasonal and spatial variability than can be explained by current models (Barkley et al., 71 2009; Alves et al., 2018; Wei et al., 2018; Gu et al., 2017; Batista et al., 2019). Isoprene's impact 72 on atmospheric oxidation has been a further subject of debate, and specifically the degree to 73 which it acts to sustain or deplete hydroxyl radical (OH) concentrations under low- NO_x 74 conditions (Lelieveld et al., 2008; Fuchs et al., 2013; Feiner et al., 2016).

75 Satellite-based measurements of isoprene are beginning to provide powerful new information for

addressing these gaps (Fu et al., 2019). Our team recently developed the first global isoprene

77 measurements from space by applying an efficient machine-learning algorithm to thermal

78 infrared radiances from the Cross-track Infrared Sounder (CrIS; Wells et al., 2020). That

approach derived isoprene column abundances from the CrIS-measured on-peak/off-peak

80 brightness temperature difference (ΔT_b) at the ν_{28} absorption feature, and showed that combining

81 these data with concurrent formaldehyde observations affords joint constraints on isoprene

82 emissions and chemistry over source regions. A major finding of that work was that the

83 isoprene:formaldehyde relationship observed from space supports current understanding of

84 isoprene-OH chemistry, with no indication of missing OH recycling at low NO_x. The new

85 measurements also pinpointed regions where emission errors for both isoprene and NO_x cause

86 major prediction biases in current models.

In this paper, we present the Retrieval of Organics from CrIS Radiances (ROCR) next-generation 87 88 isoprene retrieval, which improves on our original machine learning algorithm by employing a 89 hyperspectral range index (HRI) to quantify column abundances. The HRI approach has been used previously with the Infrared Atmospheric Sounding Interferometer (IASI) to retrieve global 90 distributions of ammonia (Whitburn et al., 2016), methanol, formic acid, peroxyacetyl nitrate 91 92 (Franco et al., 2018), acetone (Franco et al., 2019), and acetic acid (Franco et al., 2020). By 93 leveraging a broader spectral range than the brightness temperature difference, the HRI increases 94 near-surface sensitivity while reducing impacts from interferences; our updated algorithm thus 95 enables isoprene detection at unprecedented resolution while maintaining high computational efficiency. We apply the ROCR algorithm here to obtain global isoprene distributions on a daily 96 97 basis from 2012 through 2020. We evaluate the results against other observations, including the 98 first ground-based column retrievals of atmospheric isoprene, and characterize pertinent sources of measurement uncertainty. Finally, we explore this long-term global dataset, and highlight the 99 100 new, high-resolution information provided over two key isoprene hotspots.

101 2 Materials and Methods

102 CrIS is a Fourier transform spectrometer flying in a sun-synchronous orbit onboard Suomi-NPP (SNPP, launched 10/2011) and JPSS-1/NOAA-20 (launched 11/2017), with a third instrument 103 planned for inclusion on JPSS-2 (launch expected 09/2022). CrIS has 0.625 cm⁻¹ spectral 104 resolution in the longwave IR (LWIR; 650-1095 cm⁻¹), and an angular field of regard consisting 105 106 of a 3×3 pixel array with a 14-km diameter footprint at nadir and a 2200 km cross-track scan 107 width that provides near-global coverage twice daily. This sampling strategy affords the 108 opportunity for high-resolution quantification of daily isoprene distributions. The early-afternoon daytime overpass (~1330 LT for SNPP and ~1240 LT for JPSS-1/NOAA-20) typically 109 110 corresponds with peak isoprene emissions, enhanced vertical mixing, and strong land-111 atmosphere thermal contrast-all of which increase sensitivity to near-surface absorbers. CrIS 112 also features significantly lower noise (e.g., ~0.04 K at 900 cm⁻¹ and 280 K) than other 113 atmospheric sounders (Zavyalov et al., 2013).

114 2.1 CrIS HRI derivation

The ROCR algorithm derives isoprene column abundances based on the HRI (Eq. 1), which is adimensionless quantity measuring the spectral signature of a target atmospheric species (Walker

- et al., 2011). The retrieval begins with single-footprint Level 1B CrIS spectra (available from
- 118 02/2012 onward from SNPP) over land. We cloud-screen the spectra based on the difference
- between the MERRA-2 (Gelaro et al., 2017) surface temperature and the CrIS-measured 900
- 120 cm⁻¹ brightness temperature (Fig. S1), following Wells et al. (2020). The HRI is then computed
- 121 for each spectrum via (Franco et al., 2018):

122 HRI =
$$\frac{1}{N} \frac{K^T S_y^{-1}(y - \bar{y})}{\sqrt{K^T S_y^{-1} K}}$$
 (1)

123 Here, y is the measured spectrum, while \overline{y} and S_y are respectively the mean background spectrum and background covariance matrix, both calculated from scenes in which isoprene is 124 125 undetectable. $S_{\rm V}$ characterizes the expected correlations between spectral channels due to factors other than isoprene, such as interfering trace gases (Whitburn et al., 2016). K is the spectral 126 127 Jacobian for a change in the target species, which we calculate at the midpoint of 12 equallyspaced viewing angle bins (0-5° to 55-60°) using radiances generated by the Earth Limb and 128 129 Nadir Operational Retrieval (ELANOR) radiative transfer model (Clough et al., 2006) and simulated isoprene output from GEOS-Chem (v11-02e, www.geos-chem.org). The employed 130 131 spectral range (890-910 cm⁻¹) encompasses the two = CH_2 wag absorption peaks exhibited by the 132 isoprene molecule (Brauer et al., 2014).

133 The background quantities \overline{y} and S_y are calculated monthly for each angle bin from CrIS spectra that are selected iteratively following the approach used for IASI VOC retrievals (Franco et al., 134 135 2018). We start by calculating the HRI values for all spectra in a given month and angle bin. 136 After removing spectra with an HRI exceeding a specified threshold, we rederive $\overline{\mathbf{v}}$, $\mathbf{S}_{\mathbf{v}}$, and the 137 corresponding HRIs, and iterate until convergence upon a spectral ensemble with belowthreshold values. Each iteration step involves normalization (by N) to maintain an HRI mean of 138 139 0.0 and standard deviation of 1.0 for background conditions. N is calculated as the HRI standard 140 deviation over a region where target species detection is not expected; we employ spectra over central Australia (20°-30° S, 122°-137° E) for this purpose and test the use of an alternate 141 142 normalization region in Section 3.2. We achieve enhanced sensitivity for isoprene with a 143 background HRI threshold of 1.0, consistent with prior VOC findings for IASI (Franco et al., 2018); we explore the retrieval sensitivity to this threshold in Section 3.2. Once iteration is 144 complete, we generate daily gridded HRI maps at $0.5^{\circ} \times 0.625^{\circ}$ resolution. 145

146 By encompassing a broader spectral range over which the target species is optically active, the

- 147 HRI generated as above delivers improved sensitivity over ΔT_b -based and other approaches. It
- also lessens the impacts of interferents by using measured radiances to account for spectral
- 149 correlations under background conditions. Figure S2 demonstrates this improvement by
- 150 comparing the isoprene HRI and ΔT_b (at v_{28}) for synthetically-generated radiances under varying
- 151 environmental conditions and a given viewing geometry. The HRI exhibits a tighter linear
- 152 correlation with isoprene (r = 0.78 versus 0.51 in this example) with significantly less scatter for
- 153 low and moderate column densities ($\Omega_{isoprene} < 1 \times 16$ molec cm⁻²). Thermal contrast, water vapor
- and other factors still drive some variability in the HRI-isoprene relationship, and we account for
- 155 these residual effects using a neural network as described next.

156 **2.2 Machine-learning retrieval**

157 Isoprene abundances are derived from the CrIS HRIs using a feed-forward neural network (NN) as employed in our previous work (Wells et al., 2020). The NN is trained using a synthetic HRI 158 159 dataset generated from a full year of global overland ELANOR radiances simulated at the 160 midpoint of the 12 angle bins described earlier. ELANOR inputs include temperature and water 161 vapor profiles from the NASA Goddard Modeling and Assimilation Office (GMAO) and 162 isoprene profiles from GEOS-Chem (Wells et al., 2020), with the latter subjected to $100\% 1\sigma$ Gaussian noise to ensure that NN predictions reflect the spectroscopic effects of the input 163 variables rather than any prior correlations between them. We replicate the ELANOR spectral 164 165 output 25 times per scene, with CrIS-like noise applied each time, and compute the resulting 166 simulated HRIs as:

167 HRI_{sim} =
$$\frac{K^T S_y^{-1}(y - y_0)}{\sqrt{K^T S_y^{-1} K}}$$
 (2)

where y and y_o are simulated spectra with and without the target species, and S_y is the CrISobserved background spectral covariance matrix for the same month-of-year. Using spectral pairs with and without the target species for the simulated HRI reduces retrieval sensitivity to forward model errors, while preserving a mean of zero in the absence of the target gas (Franco et al., 2018). The final HRI_{sim} for each scene is obtained as the mean across the 25 replications.

We then train the NN to convert the HRI values to isoprene columns while accounting for theadditional factors that affect that relationship. For isoprene we find that these comprise water

175 vapor column, thermal contrast, surface pressure, and viewing angle. Our previous ΔT_b -based

- 176 retrieval also included nitric acid as a predictor (Wells et al., 2020), but we find here that its
- 177 inclusion does not improve predictive power, implying that its effects are already captured in the
- 178 HRI computation. Other factors found here (surface emissivity) or previously (ammonia, CFCs;
- 179 Wells et al., 2020) to confer no predictive benefit are similarly omitted.
- 180 After testing multiple architectures, we find optimum performance for a two-layer network with
- 181 10 and 5 nodes. The training proceeds on 10 random extractions of the data, with 50% of each
- extraction used for training, 30% for validation, and 20% for testing. Finally, we apply the
- resulting 10 NNs to the CrIS-measured HRIs with temperature and water information obtained
- 184 from MERRA-2 reanalysis (Gelaro et al., 2017), and derive the final retrieved isoprene column
- as the mean output across the 10 NNs.
- 186 We have applied the above ROCR algorithm to obtain global, daily distributions of isoprene at
- 187 $0.5^{\circ} \times 0.625^{\circ}$ resolution spanning most of the CrIS SNPP record (2012-2020). As we
- 188 demonstrate below, the retrieval exhibits significantly less noise than our previous version
- 189 outlined in Wells et al. (2020). We do obtain some artifacts at high latitudes that we attribute to
- 190 surface effects in the presence of ice and snow. We therefore postfilter scenes with surface
- 191 temperatures below 273 K as we do not expect to detect isoprene in such conditions; a similar
- approach is used for IASI VOC retrievals (Franco et al., 2018; Franco et al., 2019).
- 193 Next, in Section 3, we present a series of intercomparisons and sensitivity tests to characterize 194 relevant uncertainties in the ROCR isoprene retrievals. Subsequently, in Section 4 we explore the 195 spatial and temporal information provided by these new satellite-based isoprene measurements 196 over key global source regions.

197 3 Validation and error characterization

3.1 Comparison to OE and brightness-temperature difference approach

- 199 We begin with a spatial evaluation of the next-generation ROCR isoprene retrievals against
- 200 previously published results generated using optimal estimation (OE; Fu et al., 2019) and
- brightness-temperature difference (Wells et al., 2020) methods. Fig. 1 compares these three
- 202 datasets over Amazonia during September 2014. The high degree of spatial consistency (panels
- a-c) and strong correlation (r = 0.92-0.93, panels d-e) among them provides confidence in the

- 204 isoprene distribution provided by these separate approaches. Furthermore, we see reduced scatter
- at low-to-moderate isoprene for the HRI-OE comparison (Fig. 1e) compared to the ΔT_b -OE case
- 206 (Fig. S3)—demonstrating the HRI signal-to-noise improvement over the earlier ΔT_b approach.



207 ΔT_b isoprene [molec/cm²]OE isoprene [molec/cm²]208Figure 1. Isoprene retrieval comparison over Amazonia during September 2014. Maps display monthly-mean
columns averaged on a 2° × 2.5° grid and normalized to their domain means for (a) the ROCR HRI-based209retrieval, (b) the ΔT_b - based retrieval presented in Wells et al. (2020), and (c) the OE-based retrieval
presented in Fu et al. (2019). Scatter plots compare the corresponding absolute column densities. Error bars
in the scatter plots show the standard deviation across the 10 NNs; the red line and gray shaded area indicate
the reduced major axis regression and bootstrapped 95% confidence interval, respectively. The dashed line
shows the 1:1 relationship.

- 215 The major-axis intercomparison slope for the ROCR HRI-based isoprene columns is 0.81 vs. the
- 216 ΔT_b -based columns and 0.63 vs. the OE-based columns (Fig. 1d-e). As discussed by Franco et al.
- 217 (2018), each of these retrieval approaches is subject to its own uncertainties, some of which may
- 218 be systematic. In the OE case, these include forward model assumptions, fitting errors for
- 219 interfering species, and the dependence on a priori target species information. In particular, the
- 220 OE columns in Fig. 1 (Fu et al., 2019) employ isoprene columns from GEOS-Chem as prior,
- which have been shown to have a major high bias over Amazonia (Wells et al., 2020); this may
- 222 partly explain the difference seen in Fig. 1e. Uncertainties for the HRI-based approach include
- assumptions in the forward model set-up and in the HRI derivation. We examine the impact of
- these in Section 3.2, and present a comparison of the ROCR HRI-based isoprene retrievals to
- independent ground-based column observations in Section 3.3.

226 **3.2** Uncertainty analysis

- 227 We assess the uncertainties of the HRI-based results through a series of sensitivity analyses
- 228 targeting specific aspects of the retrieval. We focus in particular on the HRI background
- 229 computation, cloud screening, normalization approach, vertical mixing, and potential
- 230 interferences from monoterpenes.

231 3.2.1 Background definition

- 232 The background spectrum and covariance matrix (\bar{y}, S_y) were derived in Section 2.1 using an
- HRI < 1 threshold following Franco et al. (2018). We tested the impact of this selection by
- reanalyzing a full year of CrIS spectra with an alternate background definition (HRI < 2). The
- resulting S_v matrix was used to rederive the simulated HRI values, with the NN then retrained
- and applied to the updated CrIS HRI fields.
- Figure 2a-b compares the resulting monthly-mean isoprene columns to those obtained with our
- standard approach. The comparison slope across the entire dataset is 0.774 ± 0.002 (bootstrapped
- 239 95% confidence interval); however, differences occur primarily for points with $\Omega_{isoprene} < 1 \times$
- 10^{16} molec cm⁻². Use of a higher threshold leads to retention of more low-to-moderate isoprene
- scenes in the background calculation, yielding a negative bias at low column amounts. This
- 242 impact is strongly reduced when isoprene is elevated, with mean differences decreasing from
- 243 20% at 1×10^{16} molec cm⁻² to near-zero at higher column amounts.



244

Figure 2. ROCR isoprene sensitivity to different aspects of the retrieval: (a) Comparison of monthly-mean
isoprene columns derived with a background definition of HRI<2 against the baseline approach using HRI<1.
(c) Comparison of monthly-mean isoprene columns derived with a more stringent cloud-screening threshold

248against the baseline approach (see text). (e) Comparison of monthly-mean isoprene columns derived when249including ocean scenes against the baseline land-only approach. (g) Comparison of monthly-mean isoprene250columns derived when using an alternative PBL mixing scheme during NN training. The red and dashed lines251show the reduced major axis regression and 1:1 relationship, respectively. (b, d, f, and h) Percent difference252 $(100\% \times [\Omega_{test} - \Omega_{base}]/\Omega_{base})$ for each test as a function of the baseline column amount, with black dots253and error bars denoting the mean and standard deviation for each bin. Coloring in each panel indicates the254data density.

255 3.2.2 Cloud-screening

256 Clouds are an important consideration in thermal-IR retrievals, generally acting to reduce signal 257 by obscuring the below-cloud portion of the trace gas column (Whitburn et al., 2016). For that reason we cloud-screen the CrIS spectra as described in Section 2.1; if such screening were 258 259 inadequate we would expect a low retrieval bias due to retained cloudy scenes. To characterize the uncertainties associated with cloud-screening, we performed a sensitivity test using a more 260 261 conservative cloud threshold (based on the clear-sky difference between the 900 cm⁻¹ brightness temperature and surface skin temperature, as shown in Fig. S1). As above, we then reanalyzed a 262 year of CrIS spectra, regenerated the training set using the updated S_{ν} , retrained the NN, and 263 264 applied it to the observed HRI fields. Results plotted in Fig. 2c-d show that for all but the lowest 265 isoprene columns the impact of this alternate cloud treatment is minimal, with mean differences 266 of < 5% relative to the base-case. We conclude that clouds are not a predominant source of 267 uncertainty in these retrievals.

268 3.2.3 Inclusion of ocean scenes and HRI normalization

269 Given isoprene's terrestrial sources and short atmospheric lifetime, we restrict the base-case retrieval to land scenes for computational efficiency. The HRI normalization step, which requires 270 271 scenes lacking the target species, then employs spectra over central Australia as outlined in 272 Section 2.1. We tested the impact of this treatment by reanalyzing a year of CrIS spectra for both 273 ocean and land scenes, with HRI normalization based on spectra over the remote Pacific (10° to 30° S. 180° to 130° W) rather than Australia. Results are shown in Fig. 2e-f. Isoprene columns 274 275 derived when including vs. excluding ocean scenes generally agree to within 5-10% on average for retrievals above 0.5×10^{16} molec cm⁻², showing that this data selection criterion does not 276 277 impart significant uncertainty to the results.

278 3.2.4 Vertical mixing

279 Satellite-based measurement sensitivity in the thermal IR depends on the vertical distribution of 280 the absorber and hence on atmospheric mixing. To test the sensitivity of the retrievals to model 281 vertical mixing assumptions, we generated a new HRI training set from ELANOR simulations 282 driven by GEOS-Chem isoprene profiles produced using an alternate planetary boundary layer 283 (PBL) scheme (Wu et al., 2007). Here, all surface emissions are mixed instantaneously through 284 the vertical extent of the boundary layer, resulting in higher lofting of isoprene than in the 285 standard case, which employs the GEOS-Chem default non-local PBL mixing scheme (Lin and 286 Mcelroy, 2010). Fig. S4 compares results for these two mixing treatments over Amazonia. We 287 then trained a NN with this modified output and applied it to a year of CrIS-measured HRI 288 values.

289 Figure 2g-h shows that the resulting columns have mean differences of up to 20% between these 290 two cases, with higher columns generally obtained with the full-mixing scheme. By itself we 291 would expect the enhanced isoprene lofting to yield a higher HRI for a given isoprene 292 abundance-therefore leading to lower column predictions from the CrIS HRI fields. This is 293 indeed what occurs under dry conditions (Fig. S5). However, isoprene is predominantly emitted 294 in humid tropical climates, and under wet conditions enhanced water-driven IR absorption below 295 the lofted isoprene yields the opposite effect (the water distribution is prescribed by the 296 assimilated meteorological fields driving the simulation, and is not altered by the change in 297 mixing scheme). Overall, however, we can consider the <20% mean differences arising from this 298 sensitivity test (as shown in Fig. 2d) to reflect the envelope of uncertainty arising from vertical 299 mixing as currently represented in chemical transport models.

300 *3.2.5 Potential interference from monoterpenes*

In our previous work (Fu et al., 2019; Wells et al., 2020) we assessed the potential for other 301 302 molecules with terminal =CH₂ groups to interfere with the isoprene signal, and concluded that 303 monoterpenes are likely the most important such species to consider. To estimate the extent of 304 their potential impact, we compute and compare optical depths for isoprene and total 305 monoterpenes at the peak of the v_{28} isoprene feature. For purposes of this assessment, optical 306 depths are approximated as the product of the GEOS-Chem column densities and the 307 corresponding absorption cross sections (Gordon et al., 2017) at v_{28} and 298 K. Monoterpenes 308 are simulated in GEOS-Chem as MTPA (α -pinene + β -pinene + sabinene + carene), MTPO

309 (terpinene + terpinolene + myrcene + ocimene + other monoterpenes), and limonene. For MTPA

310 we employ the β -pinene cross-section (which is the largest reported among constituent species)

311 whereas for MTPO we employ the myrcene cross-section (the only one reported among

312 constituent species).

313 While these biogenic species share a number of emission hotspots, Fig. 3 shows that the total 314 estimated monoterpene optical depth is typically <5% that of isoprene for major isoprene source regions. The monoterpene signal only becomes relevant for isoprene columns $< 5 \times 10^{14}$ molec 315 316 cm⁻², well below the CrIS limit of detection (Wells et al., 2020). Furthermore, this influence is 317 likely to be an upper limit, for two reasons. The first is our assumption that all MTPO species 318 absorb as efficiently as β -pinene. The second is that all the published monoterpene cross sections in 890-910 cm⁻¹ (Gordon et al., 2017) are spectrally distinct from that of isoprene, diminishing 319 320 any potential impact on the HRI. We therefore consider monoterpene interferences to be minimal 321 for the isoprene retrievals shown here.



322 Isoprene column (molec/cm²)
 323 Figure 3. Potential impact of monoterpenes on the CrIS isoprene retrievals. Shown is the estimated
 324 isoprene:monoterpene optical depth ratio as a function of isoprene column. Optical depths are derived from
 325 GEOS-Chem model predictions as described in-text.

326 **3.3** Comparison to ground-based isoprene retrievals

- 327 We showed in the last section that different retrieval assumptions, particularly the HRI
- 328 background definition and vertical mixing treatment in the forward model, can each lead to
- 329 systematic uncertainties on the order of 10-20% for isoprene columns $> 1 \times 10^{16}$ molec cm⁻² (and
- 330 higher at lower column amounts). For that reason, independent evaluation is key. Here, we

- 331 compare the ROCR isoprene retrieval from CrIS against ground-based Fourier Transform
- 332 InfraRed (FTIR) isoprene column measurements at Porto Velho (8.77° S, 63.87° W), on the

border between the Brazilian states of Rondônia and Amazonas.

The ground-based instrument is a Bruker 125M high-resolution (up to 0.006 cm⁻¹) spectrometer

- previously deployed at Saint-Denis, Réunion Island (Vigouroux et al., 2009, 2012). Since 2016,
- the instrument has been used at Porto Velho for satellite validation of formaldehyde, methane,
- and carbon monoxide (Vigouroux et al., 2020; Sha et al., 2021). Measurements in the spectral
- range needed for isoprene detection started in June 2019 and ended October 2019.

339 These measurements represent the first retrievals of isoprene from ground-based FTIR spectra.

- 340 Information on retrieval settings is provided in Table 1 and we refer to Vigouroux et al. (2012)
- 341 for further details. Retrievals employ the SFIT4 algorithm commonly used in the InfraRed
- 342 Working Group of the Network for the Detection of Atmospheric Composition Change
- 343 (NDACC), with the spectral range extended to 917 cm⁻¹ to encompass the CCl_2F_2 feature
- maximum. Figure S6 shows an example of the retrieved spectral signatures. As Porto Velho is
- located in a tropical environment, the H₂O lines are very strong (Fig. S6b) and we therefore
- apply a de-weighting (Signal-to-Noise Ratio of 0 instead of 200) to some of these lines that are
- 347 not well-fitted (see residuals in Fig. S6c). The theoretical (OE) mean total random uncertainty is
- 348 approximately 7% (3.4×10^{14} molec cm⁻²) and is due primarily to temperature uncertainties
- $(\sim 6\%;$ Vigouroux et al., 2018) and measurement noise ($\sim 3\%$). The mean theoretical total
- 350 systematic uncertainty is approximately 21%, dominated by spectroscopic (~20%) and
- 351 temperature ($\sim 4\%$) components.

Figure 4a shows that the monthly-mean ground-based retrievals derived as above agree well with the CrIS observations, with both datasets exhibiting consistent seasonal increases between June and September. We also see significant CrIS-FTIR correlation on a daily timescale (r = 0.47when employing FTIR spectra within ± 2 h of the CrIS overpass), showing that both datasets are capturing short-term ambient fluctuations. The daily isoprene columns from CrIS are somewhat higher than the ground-based results (slope: 1.5; 95% confidence interval: 1.1-2.0, Fig. 4b), whereas they were somewhat lower than the previously published OE and ΔT_b retrievals shown

in Section 3.1.





360 361 Figure 4. Comparison of CrIS ROCR and ground-based FTIR isoprene retrievals at Porto Velho, Brazil for 362 June-September 2019. (a) Monthly mean (± standard deviation) isoprene columns based on the CrIS (black) 363 and ground-based (red) retrievals. (b) Daily mean CrIS vs. ground-based (±2 hours of the CrIS overpass) 364 isoprene columns; the reduced major axis regression and bootstrapped 95% confidence interval are indicated 365 by the red line and gray shaded area, respectively. The dotted line shows the 1:1 relationship.

366 The Porto Velho measurements are slated to resume in the future, and with time should provide 367 an increasingly robust resource for quantitatively testing the space-based retrievals. In theory, 368 such measurements can also be performed across the global network of ground-based solar FTIR stations (Vigouroux et al., 2020). However, this site in Amazonia is uniquely situated for the 369 370 validation of isoprene, which is measurable from space primarily over hotspot regions (Wells et 371 al., 2020).

372 4 Global distribution and key hotspot results

Figure 5 shows the global distribution of monthly-mean ROCR isoprene retrievals as a multi-373

374 year mean over the 2012-2020 SNPP CrIS record. These data represent the first space-based

- 375 quantification showing the full seasonal cycle of atmospheric isoprene. We see the highest
- columns over Amazonia, with a widespread regional maximum in September and a secondary 376
- 377 more localized maximum over northwestern Brazil peaking in April. Within the northern

378



379 380

381 CrIS, averaged from 2012-2020 for each month of the year (2013-2020 for January). Data are plotted with

382 383 partial transparency on the underlying land cover; missing data (e.g., in the wintertime high northern

latitudes) have full transparency.

midlatitudes, the highest isoprene columns occur during summer over the Ozarks region of the
US, with other summertime enhancements detected over the forests of Canada and Russia.

386 Over Africa, CrIS reveals a distinct north-south seasonal shift, with isoprene enhancements in 387 the southeast (Angola/Zambia) peaking in January-February, throughout the Sahel during May-388 October, and in central Africa during March-April and September-October. A similar seasonal 389 pattern manifests over Oceania and East Asia: during February-April the highest columns occur 390 over northern Australia, with this peak then shifting northward to Southeast Asia, eastern China, 391 and the eastern Indian subcontinent by July-September. Detection for many of the above patterns 392 is made feasible by the improved sensitivity of the HRI retrieval: over East Asia, for example, 393 the short isoprene lifetimes and lower column amounts hindered detection with the previous ΔT_b 394 approach (Wells et al., 2020).

Below, we explore these results in more detail over two key isoprene source regions—the United
States+Mexico and Amazonia—demonstrating in particular the capabilities of this new dataset
for resolving patterns of isoprene variability at high spatial resolution and on daily timescales.

398 4.1 United States and Mexico

399 Figure 6 shows the 2012-2020 ROCR isoprene retrievals over the US and Mexico averaged by month for May-October. The data exhibit strong spatial heterogeneity at unprecedented 400 401 resolution, with major hotspots over the "isoprene volcano" in the southern Missouri/northern 402 Arkansas Ozarks (Wiedinmyer et al., 2005) and over the Yucatán Peninsula in Mexico, an area 403 with some of the highest predicted emission rates globally (Opacka et al., 2021). Substantial 404 isoprene enhancements are also observed over the South-Central Plains in eastern Texas and western Louisiana, where an emission underestimate was previously inferred from satellite-based 405 406 measurements of formaldehyde (Kaiser et al., 2018). We also see elevated isoprene columns over 407 source regions along the Piedmont Plateau in Appalachia, in coastal Mexico, in the national forests of southwestern Colorado, in northern California, and in the Sierra Nevada foothills. 408



- 416 as the primary isoprene hotspot in this region. Over this hotspot, the CrIS measurements are
- 417 further able to resolve daily isoprene variability correlating strongly with surface temperature

- 418 during summer (Fig. 8), reflecting the underlying emission dependence (Guenther et al., 1993).
- 419 Quantifying this isoprene-temperature relationship on a daily basis represents a major advance
- 420 over our previous retrievals, which required monthly averaging to enhance signal-to-noise (Wells
- 421 et al., 2020). We see in Fig. 8j that the isoprene-temperature dependence seen from space by
- CrIS corroborates the bottom-up predictions, with an absolute offset consistent with the isoprene 422
- 423 lifetime underestimate inferred previously for GEOS-Chem over this region (Wells et al., 2020).



424 425

Figure 7. Spatial distribution of isoprene over the Southeast US as measured from aircraft (left) and CrIS

426 (right) during the SENEX (top, June-July 2013) and SEAC⁴RS (bottom, August-September 2013) campaigns.

427 Aircraft data are displayed as campaign mean (daytime flights only) density weighted boundary layer (P >

428 800 hPa) concentrations (molec cm⁻³); CrIS data are plotted as column densities (molec cm⁻²) averaged over

429 the flight days of each campaign. Areas in gray have no available data.



430 431 Figure 8. Daily evolution of summertime (June-September) isoprene over the US Ozarks. (a-i) CrIS isoprene 432 (black) and MERRA-2 surface air temperature (Tsfc, orange) timeseries averaged over the Ozarks region for 433 each year from 2012-2020. (j) Daily CrIS (black) and GEOS-Chem (red) isoprene columns for the same 434 region and timeframes plotted as a function of surface air temperature. An exponential fit to each data set is 435 shown with $T_o = 330$ K in each case.

436 The strong temporal isoprene variability over the Ozarks that is revealed by CrIS in Fig. 8 is

- 437 corroborated not only by the above temperature correlation but also by separate aircraft and
- ground-based observations. For example, Fig. S7 shows that day-to-day differences of 438

- 439 comparable magnitude are detected over this region from both space-based and airborne
- 440 platforms. Furthermore, the highest CrIS isoprene columns across the entire Ozark data record
- 441 occur in early July of 2012 (Fig. 8a), when anomalously large isoprene fluxes were measured in
- situ (Seco et al., 2015) during the early phase of an extreme drought.

443 **4.2 Amazonia**

- 444 Figure 9 shows CrIS isoprene columns over Amazonia averaged across the SNPP record for
- January, March, May, July, September, and November. Significant spatial variability is revealed
- by the high-resolution CrIS isoprene data over this region. The highest columns are observed
- 447 over the western Brazilian state of Acre (on the border with Peru and Bolivia), followed by a
- 448 widespread enhancement over the northern Amazon Basin (Brazilian states of Amazonas, Pará,
- 449 and Roraima) and a more localized hotspot over Maranhão in eastern Brazil. Persistently low
- 450 isoprene columns are detected along the Amazon mainstem and over other major regional
- 451 floodplains (Fig. S8; Hamilton et al., 2002), consistent with the elevational and phenological
- 452 gradients in isoprene emissions discussed by Gu et al. (2017).





- 456 Strong seasonal shifts are seen in the location and magnitude of the above isoprene
- 457 enhancements. In particular, a widespread maximum is detected during the dry season

458 (September-October) when temperatures and leaf area are highest (Wei et al., 2018). A more

- 459 localized maxima then emerges over the northwest Amazon basin during the wet season
- 460 (January-May), with a minimum during the transition between these two periods (June-July)
- 461 when leaf flushing is believed to cause a large-scale shutdown of isoprene emissions (Barkley et
- 462 al., 2009).
- 463 As was the case over the southeastern US, we also observe significant day-to-day isoprene
- 464 variability over Amazonia. Figure 10a shows an example isoprene timeline for year-2013 over
- the state of Acre in western Brazil, where the highest columns in the entire basin are often
- 466 detected. Isoprene enhancements of similar magnitude occur during both the wet and dry
- 467 seasons—despite the much higher temperatures, and thus presumably higher emissions, in the
- 468 dry season (Fig. 10c). Further, the daily isoprene columns have a robust temperature correlation
- 469 during the dry season (r = 0.58, Fig. 10c) but not during the wet season (r = 0.11, Fig. 10b) when
- 470 the temperature range is small.



471 472 Figure 10. Seasonal variability in atmospheric isoprene over the state of Acre in western Brazil as seen from 473 CrIS. (a) Temporal evolution of CrIS isoprene (black), OMI tropospheric NO₂ (×10, green; Boersma et al., 474 2017), and MERRA-2 surface temperature (orange) averaged over the region during year-2013. (b) CrIS 475 isoprene columns plotted as a function of MERRA-2 surface temperature and shaded by lifetime for the 476 Amazonian wet season (January-May) and (c) dry season (August-October). Isoprene lifetimes are derived 477 from the isoprene:HCHO column ratios as described by Wells et al. (2020) using HCHO data from OMI (De 478 Smedt et al., 2017). Exponential fits to the dry season data are shown for isoprene lifetimes < 3 h (blue), 3-6 h 479 (green), and > 6 h (orange). The timelines are displayed as a three-day running mean; scatter plots show daily 480 data.

- 481 The above patterns arise because of seasonal NO_x-driven differences in the isoprene lifetime.
- 482 Wells et al. (2020) showed previously that the isoprene lifetime can be directly estimated from
- 483 the satellite-measured isoprene:formaldehyde column ratio. Applying the same approach here,

- 484 we see that in the wet season, when NO_x is low ($< 5 \times 10^{14}$ molec cm⁻², Fig. 10a), isoprene
- 485 lifetimes over Acre are far longer (often 10-20+ h, Fig. 10b) than they are in the dry season
- 486 (typically < 6 h, Fig. 10c) when NO_x is elevated (> 1×10^{15} molec cm⁻², Fig. 10a). This
- 487 suppressed OH then leads to runaway wet season concentrations in spite of the relatively low
- 488 temperatures. Furthermore, we find during the dry season that the isoprene column:temperature
- relationship varies in a coherent way with the isoprene lifetime: when lifetimes are longer the
- 490 temperature dependence is steeper, and vice versa (Fig. 10c). This coherence further
- 491 demonstrates the fidelity of the daily CrIS isoprene measurements.

492 **5** Conclusions

493 We have described the next-generation ROCR isoprene retrieval, and applied it to obtain daily 494 global isoprene distributions from the CrIS satellite sensor for 2012-2020. The retrieval employs 495 the HRI as isoprene spectral index in a machine learning framework, building on previous work 496 for other VOCs with the IASI sensor (Franco et al., 2018; Franco et al., 2019; Franco et al., 497 2020). We show that the ROCR isoprene retrieval provides enhanced sensitivity over our 498 previous method while maintaining computational efficiency to fully exploit the dense global 499 sampling of the CrIS instruments. Over Amazonia, the spatial distribution of the new isoprene retrievals is highly consistent with prior OE and ΔT_b -based results, with daily variability that 500 501 compares well with ground-based column observations. The derived CrIS isoprene columns are 502 lower in magnitude (20-40%) than earlier retrieval versions but higher (up to 50% for daily data) 503 than the ground-based results, likely reflecting different sources of systematic uncertainty in the 504 various approaches. A series of sensitivity tests identifies the background definition and isoprene 505 vertical profile as the most relevant uncertainty sources in the ROCR retrieval. Independent 506 validation continues to be a critical need for robust interpretation of the isoprene column 507 abundances in terms of controlling process.

The long-term global CrIS dataset presented here has unprecedented resolution, revealing strong seasonal and spatial variability in atmospheric isoprene. Clear seasonal cycles are seen over the world's isoprene hotspots, including East Asia and India where sensitivity was limited with our previous approach. Over the US and Mexico, isoprene enhancements are observed across a range of ecosystems and in particular over the "isoprene volcano" in the Ozarks. There, the patterns of variability detected by CrIS are supported by independent data, reflecting emission drivers on 514 daily (e.g., temperature) to interannual (e.g., drought stress) timescales. Over Amazonia, strong

spatial gradients are observed that vary temporally according to seasonal phenology of the

516 underlying landscape features. Combining the CrIS data with space-based formaldehyde and

517 NO₂ measurements reveals daily lifetime variations that elucidate the dual controls of emissions

518 and chemistry on the isoprene abundance.

519 Overall, results presented here demonstrate the ability of these high-resolution CrIS retrievals to 520 resolve daily isoprene variability from space, thus enabling new investigations into emission 521 processes across a range of plant functional types. Our initial analyses highlighted some of the emergent connections between isoprene abundance and daily-to-interannual variations in 522 523 temperature, NO_x, and drought stress. Because the CrIS record is planned to extend through at 524 least 2030, the ROCR isoprene retrievals will provide valuable long-term information for 525 diagnosing ecosystem variability and the links between surface-atmosphere exchange, climate, 526 and chemistry in biogenic source regions.

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539 Open Research

540 The CrIS Level 1B data used in this work are publicly available at https://snpp-

541 sounder.gesdisc.eosdis.nasa.gov/data/SNPP_Sounder_Level1/SNPPCrISL1BNSR.2/. The ROCR

isoprene column data analyzed here are available at http://z.umn.edu/ROCR_isoprene. Employed

- 543 airborne data is publicly available at http://esrl.noaa.gov/csd/projects/senex/ (SENEX) and at
- 544 http://www-air.larc.nasa.gov/missions/seac4rs/index.html (SEAC⁴RS). GEOS-Chem model code
- 545 is available at www.geos-chem.org.
- 546

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713	Table 1: Settings for the ground-based FTIR isoprene retrievals at Porto Velho.
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Retrieval code	SFIT4v09.4.4; available at https://www2.acom.ucar.edu/irwg/
Spectral window	891.6-917.0 cm ⁻¹
De-weighted signatures (H ₂ O)	896.4-896.6; 897.6-897.8; 902-8-903.2; 906.5-907.0; 907.7-908.9;
	910.1-910.4; 910.6-910.8; 911.2-911.3; 914.5-915.0 cm ⁻¹
Retrieved species (target +	Profile retrieval: C ₅ H ₈ , H ₂ O, NH ₃
interfering)	Scaling of the a priori profile: CO ₂ , HNO ₃ , H ₂ ¹⁸ O, C ₂ H ₄ , CCl ₂ F ₂ ,
	F142b, solar CO
Spectroscopic parameters	C ₅ H ₈ : pseudo line list by G. Toon (JPL):
	https://mark4sun.jpl.nasa.gov/pseudo.html, constructed from the
	cross-sections of Brauer et al. (2014).
	H_2O , $H_2^{18}O$: from Toth (2003), available at
	http://mark4sun.jpl.nasa.gov/data/spec/H2O/RAToth_H2O.tar
	NH ₃ , HNO ₃ , C ₂ H ₄ : HITRAN 2012
	CO ₂ : HITRAN 2008
	CCl ₂ F ₂ , F142b: pseudo line list by G. Toon (JPL)
	Solar CO: updated from Hase et al. (2010), see SFIT4v09.4.4
	package.
A priori profiles of atmospheric	H_2O , $H_2^{18}O$: 6-hourly profiles from NCEP
species	Other species: climatology from WACCM v4 model
P, T profiles	6-hourly profiles from NCEP
Regularization	Tikhonov L1 regularization (Tikhonov, 1963; see also Vigouroux et
	al., 2012 for application to FTIR); α -value = 50, 5, and 0.1 for C ₅ H ₈ ,
	H ₂ O and NH ₃ , respectively.
Uncertainties	Random: 7% (3.4×10^{14} molec/cm ²); Systematic: 21%