# The Ultraviolet Environment of a Tropical Megacity in Transition: Mexico City 2000-2019

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1 Abstract

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Tropical regions experience naturally high levels of UV radiation, but urban pollution can reduce these levels substantially. We analyzed 20 years of measurements of the UV Index (UVI) at several ground-level locations in the Mexico City Metropolitan Area and compared these with UVI values estimated from satellite overpasses observing ozone and clouds (but not local pollution). The ground-based measurements were systematically lower than the satellite-based estimates, by ca. 35% in 2000 and 20% in 2019. Calculations with a radiative transfer model and observed concentrations of air

pollutants explained well the difference between satellite- and ground-based UVI, and showed specific contributions from boundary layer and free trophosperic aerosols, O<sub>3</sub>, NO<sub>2</sub>, and SO<sub>2</sub>, in decreasing order of importance. Such large changes in UV radiation between 2000 and 2019 have important implications ranging from human health (skin cancer and cataract induction) to air pollution control (photochemical smog formation).

Ultraviolet (UV) radiation is an important component of the urban environment, affecting

#### 4 Introduction

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human populations directly through UV exposure of skin and eyes 1-3 and less directly (but 16 with great impact) by driving the formation of photochemical smog, including tropospheric 17 ozone and other oxidants, as well as secondary aerosols containing nitrates, sulfates, and 18 organics. 4-6 These pollutants, along with others of primary origin commonly found in ur-19 ban atmospheres (e.g., black carbon, sulfur dioxide), can in turn scatter and/or absorb UV 20 radiation, alter its vertical distribution, and so modify the photochemical rate of their own 21 formation. Such feedback complicates the calculation of both the UV radiation field (including at the surface), and the evolution of photochemical smog in the urban boundary 23 layer. 24 The question of how air pollution alters the urban UV environment (and vice versa) is 25 not new, but studies have relied mostly on numerical models, <sup>7-9</sup> with relatively fewer available observations (e.g., McKenzie et al. 10, Panicker et al. 11, Palancar et al. 12, reviewed by Bais et al. 13). Increases in UV have been estimated in association with decadal emission reductions, e.g. in China, <sup>14–16</sup> and that have led to less-than-expected reductions in photochemical smog, in part due to stronger UV photochemistry. 17-19 Emission reductions have also occurred globally during the 2020 COVID-19 pandemic, <sup>20,21</sup> but ground-level ozone in 31 some polluted areas has actually increased, <sup>22,23</sup> due at least in part to the increased UV radiation. Unfortunately, the observational data base of relevant UV radiation remains rather 33 sparse to evaluate such model-derived hypotheses.

The environment of Mexico City is of particular interest for several reasons: (1) Nearly 35 23 million people inhabit the Mexico City Metropolitan Area (MCMA), and the UV environ-36 ment has direct implications for their health, both in terms of skin/eye UV exposure and via 37 photochemical smog formation. (2) As a tropical megacity, it is to some extent representative 38 of the situation of many others, with year-round intense midday UV irradiance, a shallower 39 atmosphere due to the city's high elevation of 2240 m above sea level, and a transition to-40 ward newer and cleaner technologies, leading to gradual improvements in air quality. (3) Air 41 quality within MCMA has undergone extensive scrutiny, with a well-established monitoring 42 network since 1986,<sup>24</sup> numerous intensive field campaigns to study the meteorology, emissions, and photochemistry of smog formation, <sup>25–27</sup> and numerical modeling incorporating the evolving knowledge. <sup>28-31</sup> This extensive body of knowledge provides the foundation for understanding our study. 46 Here, we analyze two decades of continuous measurements of the UV Index at multiple 47

Here, we analyze two decades of continuous measurements of the UV Index at multiple locations within the MCMA, collected by the Secretariat of the Environment (Secretaria del Medio Ambiente, SEDEMA)<sup>1</sup> of the Mexico City government as part of an intensive monitoring network over the MCMA. The UV Index is defined as:

$$UVI = 40 \int_{250nm}^{400nm} E(\lambda, t) \cdot S_{er}(\lambda) d\lambda$$
 (1)

where  $E(\lambda, t)$  is the solar spectral irradiance in units of W·m<sup>-2</sup>·nm<sup>-1</sup> and  $S_{er}(\lambda)$  is the erythemal sensitivity of human skin. <sup>32,33</sup> Multiplication by 40 was chosen historically to express the UVI in small integer numbers, but is otherwise scientifically arbitrary.

The UVI is recognized by the World Health and Meteorological Organizations (WHO and WMO) as a standardized metric of UV radiation <sup>32</sup> for global public information. An advantage of using the UVI as (one) metric of UV radiation is that it is being increasingly observed or calculated and disseminated, enabling more objective comparisons among seasons and locations. The UVI observations from Mexico City, considered here, are an important

<sup>1</sup>https://www.sedema.cdmx.gob.mx/

element of this global picture.

While the UVI at the surface cannot be translated directly into photolysis frequencies for various photo-labile molecules, the spectral weighting of the UVI (ca. 300-320 nm) is approximately similar to that for the photolysis of ozone to singlet oxygen atoms. Other UV wavelengths are of course also important, e.g. for the photolysis of nitrogen dioxide, and may be affected differently depending on the pollutant. With these considerations and a few other caveats, UVI trends examined here can also be used to infer accompanying trends in photolysis frequencies and influences on photochemical smog formation.

#### 67 Methods

#### 68 Ground-based measurements

The Mexico City Metropolitan Area is located at 19.4°N, 99.1°W, 2240 meters above sea level (asl), surrounded by mountain ridges exceeding 5000 m asl, with complex topography and thermal inversions that inhibit winds and favor intense air pollution. 34-36 Air quality 71 monitoring and surface meteorological measurements in the MCMA are conducted continuously by the Automated Atmospheric Monitoring Network (RAMA, by its Spanish acronym) of the Atmospheric Monitoring System (SIMAT, by its Spanish acronym) of the Mexico City government. Since the year 2000, UV radiometers (model 501-A, Solar Light Company Inc., Glenside, PA) detecting wavelengths between 280-400 nm have been measuring erythemallyweighted solar radiation. The calibration of the UV sensors was carried out annually by 77 comparing against a factory-calibrated reference sensor. The output voltages from the mea-78 suring sensors were compared during at least one week against the UV readings from the 79 reference sensor to derive the calibration factor. New calibration factors typically differed 80 from the old ones by 2% or less. Reference sensors were also calibrated by the manufacturer 81 and updated periodically (between 3 to 5 years) to avoid any bias due to aging. Long term calibration drift was avoided by the yearly re-calibrations. Although at the beginning only a few stations were in operation and have been changing, currently 11 stations are recording erythemal irradiances, which are then multiplied by 40 (see Eq. 1) to give UV Indices.
Table 1 describes the location of the stations where UV Index has been measured. Figure 1
shows how the radiometers of the SIMAT have been distributed over MCMA, prioritizing
the sites with more density of population. Near real-time data for each station are available
on the SIMAT official website http://www.aire.cdmx.gob.mx/default.php. Daily maximum values (UVI<sub>max</sub>) were extracted from each of the stations around solar noon from the
time interval from 11:00 h-15:00 h CST (Central Standard Time). This database with 7305
continuous days of measurements during the period 2000-2019 was analyzed.

Table 1: SIMAT stations, environmental descriptors and geographical positions. Abbreviations names: Chalco (CHA), Cuautitlán (CUT), FES Acatlán (FAC), Hangares (HAN), Laboratorio de Análisis Ambiental (LAA), Merced (MER), Montecillo (MON), Milpa Alta (MPA), Pedregal (PED), San Agustín (SAG), Santa Fe (SFE), National Autonomous University of Mexico (UNAM) and Tlalnepantla (TLA).

Station	Environment	Lat ( <sup>o</sup> N)	Lon $({}^{\Omega}W)$	El (masl)
СНО	semi-urban zone	19.27	98.89	2253
CUT	ecological park	19.72	99.20	2263
FAC	urban	19.48	99.24	2299
HAN	urban	19.42	99.08	2235
LAA	urban	19.48	99.15	2255
MER	downtown	19.42	99.12	2245
MON	rural	19.46	98.90	2252
MPA	rural	19.18	98.99	2594
PED	residential	19.33	99.20	2326
SAG	urban	19.53	99.03	2241
SFE	residential	19.36	99.26	2599
TLA	urban	19.53	99.20	2311
UNAM	University city	19.33	99.18	2294

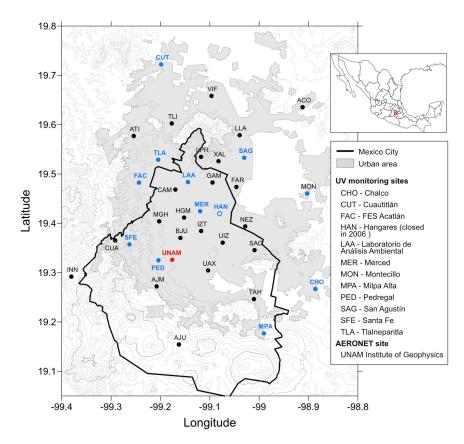


Figure 1: Map with the location of the SIMAT continuous monitoring stations over MCMA. Sites denoted by the blue solid dots correspond to SIMAT stations with UV measurements, while the black dots indicate SIMAT stations without UV measurements, the site on open blue dot represents a discontinued site, the red dot corresponds to the location of the AERONET site. The location of Mexico City and the acronyms of the UV and AERONET site are shown at the upper and lower frames at the right respectively.

With the aim to explore the relationship between UVI and air pollutants levels, the 93 hourly averages for ozone  $(O_3)$ , carbon monoxide (CO), nitrogen dioxide  $(NO_2)$ , sulfur diox-94 ide (SO<sub>2</sub>) and particle matter with diameter sizes  $\leq 10~\mu m$  (PM<sub>10</sub>), were downloaded from 95 the SIMAT.<sup>37</sup> For purposes of assessing the influence on the UV Index at solar noon, only 96 values obtained between 11h and 15h CST were considered for the trends analysis. Pollu-97 tant measurements are conducted by the SIMAT using regulatory-grade commercial instru-98 ments. Measurement principles include ultraviolet photometry (model 400E, Teledyne-API) gg for O<sub>3</sub>, chemiluminescence (model 200E, Teledyne-API) for NO<sub>2</sub>, UV fluorescence (model 100 100E, Teledyne API) for SO<sub>2</sub>, and infrared absorption (model 300E, Teledyne-API) for CO. 101

The PM<sub>10</sub> continuous mass concentration was measured with Tapered Element Oscillating Microbalance (TEOM 1400AB or TEOM 1405 DF, Thermo Scientific) monitors. Gaseous 103 pollutant levels are reported in ppb concentration units for O<sub>3</sub>, SO<sub>2</sub> and NO<sub>2</sub>, and in ppm 104 for CO. Particulate matter mass concentration is reported in  $\mu g$  m<sup>-3</sup> at local conditions for 105 temperature and pressure. 106

Aerosol optical depth at 340 nm was obtained from the Institute of Geophysics of the 107 National Autonomous University of Mexico (UNAM); measurements were conducted with 108 a CIMEL sun photometer model CE-318, which is an automatic sun-sky-scanning spectral 109 radiometer of the AErosol RObotic NETwork (AERONET<sup>38</sup>). The data Product Level 2.0 110 and 1.5 (only in 2019) were selected, and annual averages AOD<sub>340</sub> were calculated from 111 continuous measurements during at least 7 months. A previous study of the AOD behavior 112 from 2000 to 2014 demonstrated that the gaps of data did not significantly change the trends 113 over the analyzed period.<sup>39</sup> From 2014 to 2019 there was only 8% of the missing data, when 114 the instrument was sent for calibration in 2018. 115

#### Satellite data 116

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Estimates of the UV Index from satellite-based measurements of clouds and  $O_3$  were used 117 for comparing to the ground-based measurements. These data were provided by the Ozone 118 Monitoring Instrument (OMI) on board of AURA-NASA satellite. 40 OMI was created in co-119 operation between the Netherlands Agency for Aerospace Programmes (NIVR), the Finnish 120 Meteorological Institute (FMI) and NASA. OMI (hereafter OMI-Aura/NIVR-FMI-NASA) 121 performs observations over a geographical dimension of 13×24km<sup>2</sup> at nadir. For Mexico 122 City, the satellite overpass time is between 19:00h - 21:00h UTC and data are specific for 123 the coordinates and elevation of Mexico City. Measurements of the ozone profile and cloud 124 cover are used via a radiative transfer model to estimate the UVI at the ground. The OMI 125 web site reports UVI values for both the overpass time, and corrected to local solar noon. 126 While the early OMI estimates of the UVI did not consider aerosols in the boundary layer, Arola et al. <sup>41</sup> suggested correcting the clean-skies UV index with a reduction factor based on a monthly global climatology of BL aerosols. For Mexico City a reduction of about 8% is applied, starting ca. 2013, to the OMI UVI data.

#### 131 TUV model

Calculations of the UV Index were also made with the Tropospheric Ultraviolet Visible (TUV v5.3) model. <sup>42</sup> The model atmosphere was represented by 80 vertical layers, each 1 km thick, starting at the 2.24 km asl elevation of MCMA, and for which the first three km constitute the atmospheric boundary layer (BL). <sup>43</sup> The ozone profile above the BL is from the US Standard Atmosphere, but rescaled to a value of 259.6 DU. Totals including the BL contributions (of 13.7 DU in the year 2000 and 9.8 DU in 2019, see below) were 273.1 DU in 2000 and 269.2 DU. The climatological O<sub>3</sub> column for this latitude and season is about 270 DU (plus or minus ca. 5 DU) so in good agreement with the values used here.

Pollutants within the BL (including O<sub>3</sub>) are assumed to be well mixed, in agreement with observations from the MILAGRO field campaign that showed the disappearance of vertical gradients in the profiles of gases <sup>44,45</sup> and aerosols <sup>46,47</sup> by late morning. The UV-absorbing gases considered here are O<sub>3</sub>, NO<sub>2</sub>, and SO<sub>2</sub>, specified in ppb.

BL aerosols are modeled by prescribing the AOD at 340 nm (from AERONET observations), scaled to other wavelengths inversely with wavelength (Angstrom coefficient = 1.0), asymmetry factor of 0.7, and a single scattering albedo of 0.85 at UV wavelengths, following the determinations made in Mexico City by Corr et al. 48 and Palancar et al. 12.

Above the atmospheric boundary layer, the model was taken to be free of aerosols, NO<sub>2</sub>, or SO<sub>2</sub>. In one sensitivity study, a total AOD of 0.7 was redistributed placing 0.2 in the free troposphere (decreasing vertically with an exponential scale height of 4 km, and 0.5 remaining in the BL). The calculated UVI differed by less than 1%. Thus, as long as the total AOD is known, knowledge of the exact vertical aerosol profile is not critical towards ground-level UVI – but would obviously affect the vertical structure of photolysis frequencies.

Radiative transfer calculations were carried out with the pseudo-spherical 4-stream option, at 1 nm steps between 280 and 400 nm.

#### 156 Results and Discussion

Figure 2 shows the diurnal variation of the UVI for several specific cloud-free days, for different seasons and several locations (CHO, MER, MON, PED, SAG, SFE and TLA). 158 UV Index from TUV model was used as reference of the behavior under clear sky days. 159 According to the comparison of measurements minute by minute, the dates with prolonged 160 fluctuations along the day were discarded. However, during the rainy period (from June 161 to October) at least a brief clouds presence is common, as shown at CHO station around 162 noon in 13 June 2017. Peak values range from 8 during autumn/winter to above 12 in 163 spring/summer, in correspondence to the respective December and June solstices. Although 164 the stations are all within a 25 km radius, substantial differences among them are notable. 165 Survey of the locations revealed that shadowing from nearby structures is not an issue. The 166 good agreement in the morning, followed by more divergence in the afternoon, is consistent 167 with the development of photo-chemical pollution hotspots during the day. Previous studies 168 (e.g., Castro et al. <sup>49</sup> and Palancar et al. <sup>12</sup>) have shown that surface UV radiation in Mexico 169 City is attenuated significantly by aerosols. The measurements shown in Fig. 2 are consistent with this increasing pollution during the course of the day, with highest aerosol loading (and 171 highest variability) attained in the afternoon. Further support for the role of pollution in suppressing the UVI comes from the observation made at the Santa Fe (SFE) site which in 173 Fig. 2 are seen to be systematically higher, e.g. by over 10% in autumn afternoons, compared 174 to the other stations. The SFE station is displaced to the west from the majority of the 175 other stations, and remains in the outskirts. This site is also approximately 300 m higher 176 than Mexico City downtown, so that the cleaner atmosphere results from both vertical and 177 horizontal variations in pollution levels. <sup>50</sup> It is indeed expected to have higher values of the UVI, in agreement with the observations.

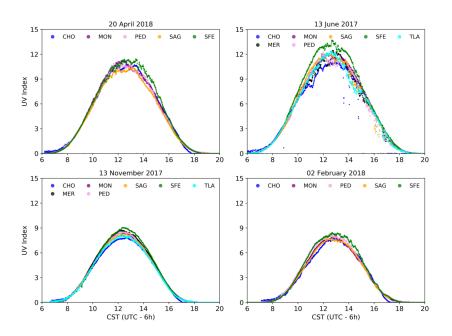


Figure 2: UV Index measured over MCMA by SIMAT stations each minute along the day under practically cloudless conditions for representative days of the year.

The daily maximum UV Index of each station is denoted by  $UVI_{\text{max}}$ , all of them were counted in the period 2000-2019. As shown in Figure 3, these values ranged from 1 to 16, with a majority (61%) of the days experienced  $UVI_{\text{max}}$  values between 6 and 10, and remarkably few, less than 1%, in the higher 13-16 range. The lowest values are likely due to winter days with heavy cloud cover and low sun angles, and UV attenuation by pollutants could also be amplified under such conditions, due to longer photon path lengths at low sun and within clouds. The extreme sparsity of high UVI values remains surprising, and may be an indication of the rarity of extremely unpolluted days within the city.

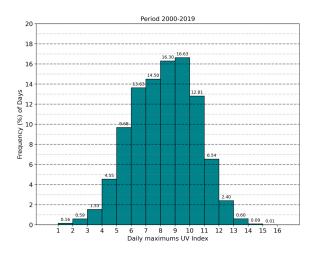


Figure 3: Frequency distribution of daily maximums UV Index values in Mexico City during 2000 -2019.

Similar patterns are found when considering the monthly average of the  $UVI_{max}$  values 188 as shown in Figure 4. The long-term averages present a seasonal variation (as in Fig. 2) 189 that follows approximately the cosine of the noontime solar zenith angle. Notably, values 190 rarely if ever exceed 12 (as in Fig. 3). The lowest average UVI (near 7) take place in winter 191 while from March to August the values seem to be flattened in the range 10-11. The rather 192 low monthly UV Index values, mainly could be a consequence of the presence of clouds in 193 the rainy season. However, urban aerosol pollution sources, biomass burning for agriculture 194 and wood cooking also contribute to poor air quality between March-May<sup>51</sup>. Using the 195 maximum  $UVI_{\text{max}}$  from all of stations every day (one daily point), the monthly averages 196  $(\overline{UVI}_m)$  were calculated along the period 2000-2019. Long term trends in  $\overline{UVI}_m$  are shown 197 in Figure 5. A clear upward trend is seen, with a slope for the linear fit of 0.9%/year or +1.5198 UVI units over the two decades. 199

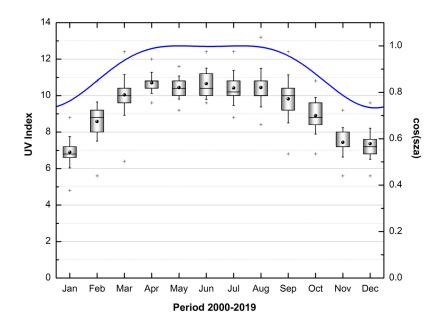


Figure 4: Boxplot of the monthly averages of the maximum UV Index values (black dot) in MCMA for the period 2000-2019: median (central bold line), 25<sup>th</sup> and 75<sup>th</sup> percentiles (box edges), standard deviation (the whiskers), the minimum and maximum values (plus sign) and the cosine of the solar zenith angle at solar noon (blue curve).

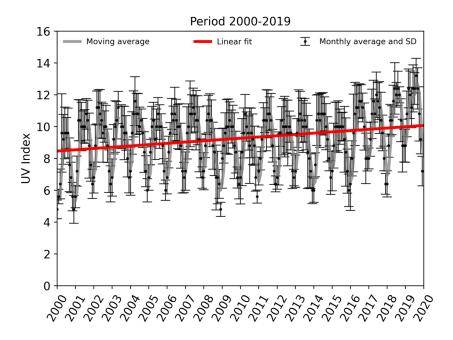


Figure 5: Moving average function (light gray curve) quarterly applied to monthly average UV Index, standard deviation of all data within a given month (black dots and dash line) and linear fit (red line).

The UV Index computed from satellite-based observations (OMI-Aura/NIVR-FMI-NASA) 200 over the period 2005-2019 is mapped in Figure 6. The satellite-derived UVIs vary from 8 201 in winter to 16 in summer, both values being substantially higher than the ground-based 202 observations (ca. 7 for winter and 11 for summer, see Fig. 4). We hypothesize that this large 203 difference between satellite-based estimation and ground-based observation of the UV index 204 is due to the intense air pollution of Mexico City. A rather similar behavior was detected in 205 Santiago city, Chile. 52 206 Close inspection of Figure 6 shows that the maximum values, those from June and July of 207 each year, show a slight but systematic decrease starting ca. 2013. As mentioned in section 208 Methods, this is due to the post-processing of OMI UVI data to account for absorption by 209

BL aerosols<sup>41</sup>, using a climatological reduction of about 8% for Mexico City.

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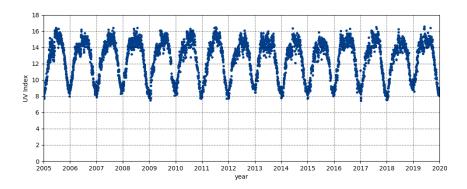


Figure 6: UV Index at solar noon for clear sky recorded by OMI-Aura/NIVR-FMI-NASA, from 2005 to 2019.

#### 211 Effect of pollutants on UV radiation

Trends and averages in aerosol optical depth  $AOD_{340}$  and criteria pollutants  $PM_{10}$ , CO,  $NO_2$ ,  $O_3$  and  $SO_2$  observed at the SIMAT stations over 2000-2019, are shown in Figure 7 and summarized in Table 2 together with the  $UVI_{max}$ . Similar trends in pollutants have been noted before  $^{53-55}$  and reflect the long-term success of emission reduction policies and programs.

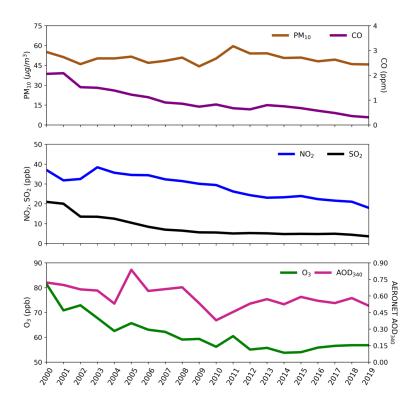


Figure 7: Air quality trends in MCMA for the period 2000-2019 from annual averages obtained between 11h to 15h CST every day:  $PM_{10}$  (brown curve), CO (purple curve),  $NO_2$  (blue curve),  $SO_2$ (black curve),  $O_3$  (green curve) and  $AOD_{340}$  (pink curve).

Table 2: UV Index and criteria pollutants: slope for the period 2000-2019, averages in units of  $\mu g/m^3(PM_{10})$ , ppm (CO), ppb (SO<sub>2</sub>, NO<sub>2</sub> and O<sub>3</sub>), dimensionless (UV Index and AOD<sub>340</sub>) and annual percentage change (%/year).

Variable	$\frac{\Delta variable}{\Delta t}$	Avg <sub>2000-2019</sub>	$\Delta(\%/year)$
UVI	0.08	9.2	0.9
$PM_{10}$	-0.10	50.2	-0.2
CO	-0.08	1.0	-8.2
$NO_2$	-0.96	28.6	-3.4
$O_3$	-1.05	61.3	-1.7
$AOD_{340}$	-0.01	0.6	-1.6
$SO_2$	-0.76	8.4	-9.1

The observed changes in the concentrations of these air pollutants have significant implications for surface UV radiation, as can be demonstrated with the TUV radiative transfer model. Table 3 summarizes UVI values for the June-July time period, estimated by the

three methods: OMI satellite-derived UVI, RAMA ground-based observations, and TUV modeling using air pollution estimates. Two groups of values can be readily identified: (1) 221 RAMA daily record values, OMI with or without BL aerosols, and TUV for very clean con-222 ditions, all with UVI values around 15-16; and (2) RAMA average daily maxima and TUV 223 UVI using MCMA pollutants as input, which are in good agreement for both 2018/19 and 224 2000/01 but much lower than the first group. Compared to the OMI estimate that included 225 the climatological aerosol correction (15.3), observed RAMA values were lower by 35% in 226 2000 and by 20% in 2019. Similarly, TUV values were 35% lower in 2000 and 22% lower in 227 2019 relative to the TUV values of 15.6 for a pristine atmosphere. 228

Table 3: UV Index monthly maximum estimates for June-July.

Conditions for estimation in June-July	UV Index
RAMA maximum reached in period 2000-2019	15.0
RAMA average maxima 2018, 2019	12.3
RAMA average maxima 2000, 2001	9.9
OMI clear, local noon, no corrected for BL aerosols	16.6
OMI with 8% reduction for BL aerosol (Figure 1 from Arola et al.)	15.3
TUV "zero" pollution	16.1
$AOD 0, O_3 0 ppb, NO_2 0 ppb, SO_2 0 ppb$	10.1
TUV pristine pollution	15.6
AOD $0.05$ , $O_3$ $10$ ppb, $NO_2$ $0$ ppb, $SO_2$ $0$ ppb	15.0
TUV 2019:	12.1
AOD 0.5, $O_3$ 50 ppb, $NO_2$ 20 ppb, $SO_2$ 1 ppb	12.1
TUV 2000:	10.2
AOD $0.7$ , $O_3$ 70 ppb, $NO_2$ 40 ppb, $SO_2$ 20 ppb	10.2

The agreement between RAMA observations and TUV model estimates is excellent but also probably a bit fortuitous. Clouds on average reduce the irradiance impingent on the surface, but scattering from them can also cause transient enhancements (especially if the direct sunbeam is not blocked) that could be recorded as daily maxima – with cancellation between these cloud effects resulting in improved agreement with the cloud-free model. We cannot exclude that some of the observed trend in UVI is due to changes in cloud cover. However, the modeled fractional UVI reductions due to pollutants, shown in Table 3, are in

such good agreement with the observed UVI reductions, that a compelling case can be made
for a dominant role of air pollutants in the long-term UVI trends.

Table 4 shows the contributions to UVI reductions from individual pollutants. Aerosols are seen to be the major factor in both time periods, followed by O<sub>3</sub>, NO<sub>2</sub>, and SO<sub>2</sub>. The 2000-2019 UVI increase is seen to result in comparable proportions from fewer aerosols, less SO<sub>2</sub>, and the combined reductions in O<sub>3</sub> and NO<sub>2</sub>.

Comparable UV reductions, of 30-40% due to aerosols, were reported by Panicker et al. <sup>11</sup>
over Pune, India from April 2004 to March 2005, with sensitivity coefficients (i.e. change in
UVI per unit change in AOD) similar to those found here in Table 3.

Comparisons of OMI with ground-based UV measurements have been reviewed recently 245 by Zhang et al. <sup>56</sup> and Vitt et al. <sup>57</sup>. OMI-derived UV generally overestimates ground-level 246 measurements by 1-10% in relatively clean conditions (e.g. rural U.S), by 10-30% in Southern 247 Europe and by 40% or more in Santiago, Chile <sup>52</sup> and Thailand <sup>58</sup>. The overestimations appear 248 related in large part to incomplete accounting of UV absorption by BL aerosol, although 249 other factors such as the correction to solar noon may also introduce some bias. 56 Over 250 Europe, ground-based UVI observations for several decades are systematically lower than 251 those estimated from satellites even after consideration of climatological aerosol distributions, showing the importance of local pollution not resolved from space.<sup>57</sup> However, difference 253 between satellite-derived and ground-based UVI was less than 1.0 UVI units in over 90% of 254 the cases, in contrast to the difference of 3-5 units found for Mexico City (Table 3). 255

UV reductions by air pollutants are expected to be most severe near the surface, while
chemical reactions leading to photochemical smog occur through the vertical extent of the
BL. Figure 8 shows the vertical profiles of photolysis coefficients (the reciprocals of photolytic
lifetimes) for two key reactions, the photolysis of O<sub>3</sub> to yield excited oxygen atoms O(1D),
and the photolysis of NO<sub>2</sub>. In the absence of optically active pollutants, these coefficients
would be nearly independent of altitude in the BL. However, the presence of pollutants
leads to a strong decrease toward the surface, with notably more severe reductions in 2000

compared to 2019. While the specific values shown in the figure are only illustrative for typical conditions, routine daily air quality modeling should carefully account for the long term variations in these photolysis coefficients.

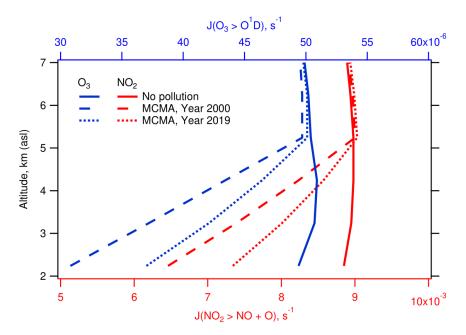


Figure 8: Vertical profiles of the photolysis coefficients for the reaction  $O_3 + h\nu \rightarrow O(1D) + O_2$  (top axis, blue)  $NO_2 + h\nu \rightarrow O + NO$  (bottom axis, red) for zero pollution (solid) and Mexico City in the years 2000 (dashed) and 2019 (dotted)

An issue that is beginning to gain relevance in radiative balance models is the influence 266 of a group of organic compounds capable of strongly absorbing in the UV region (brown 267 carbon).<sup>59</sup> Some of these compounds are related with emissions from local and regional 268 wildfires. 60 Mexico City is frequently exposed to regional fire smoke transport during the 269 dry part of the year (November to May)<sup>61</sup>, that sporadically modify the optical properties of 270 the aerosols.  $^{62}$  This could partly explain the relatively minor reductions in PM<sub>10</sub> (see Fig. 7), 271 compared to the larger reductions of CO, NO<sub>2</sub>, and O<sub>3</sub> that are more directly related to urban 272 activities, as well as some of the seasonal asymmetry seen in Fig. 3. 273 274

The UVI is specific to wavelengths mainly in the 300-320 nm range, and so the question remains whether these results can be applied at longer UV wavelengths, e.g. those important for NO<sub>2</sub> photolysis (<420 nm). Absorption by SO<sub>2</sub> and O<sub>3</sub> vanishes, while absorption by NO<sub>2</sub>

increases and typical aerosols optical depth decrease. These changes can easily be modeled, but unfortunately far fewer measurements of these longer wavelengths are available in Mexico City or elsewhere.

Two decades of observations in Mexico City demonstrate unequivocally that air pollution 280 reduces UV radiation at the ground. The ground-based observations are well below estimates 281 derived from satellite-based observations, and below model calculations do not consider 282 optically important pollutant aerosols, tropospheric ozone, and to a lesser extent NO<sub>2</sub> and 283 SO<sub>2</sub>. When typical observed values of these pollutants are included in a model (e.g. TUV), 284 the differences between satellite-derived and ground-based measured values are explained and 285 can be attributed quantitatively to individual observed pollutants. Long term improvements 286 in air quality, over two decades, are accompanied by statistically significant increases in the 287 observed UVI, again in good agreement with the model-predicted changes. 288

Table 4: Contributions of individual pollutants to UV Index changes. (a) Values used one at the time, with the others held at zero. (b) UVI deviation from the zero-pollution value of 16.1 (from Table 3). (c) 2019-2000 UVI change due to changes in each pollutant.

Pollutant	Year 2000		Year 2019		2019-2000
1 onutant	poll. level (a)	UVI (b)	poll. level	UVI	(c)
AOD	0.7	-3.7	0.5	-2.7	1.0
$O_3 \text{ ppb } (DU)$	70 (14)	-1.4	50 (10)	-1.0	0.4
$NO_2$ ppb	40	-0.9	20	-0.5	0.4
$SO_2$ ppb	30	-0.8	1	-0.04	0.8

The reductions in surface UV radiation with respect to an ideally clear atmosphere – 289 by nearly 40% in 2000 and still 20% in 2020 – are large, both within the context of hu-290 man UV exposure and air quality mitigation. In urban areas where ozone production scales 291 proportionally with UV levels and with volatile organic compound (VOC) emissions (the 292 VOC-limited regime), a 10% increase in BL average photolysis rates means that VOC emis-293 sions will need to be reduced by 10% to meet the same goals, or else successful reductions in 294 aerosols would lead to unwanted UV-driven increases in O<sub>3</sub>. Such UV changes must be con-295 sidered carefully in air quality mitigation strategies. For human exposure, a 20% increase in 296

UV irradiances over two decades should be seen as a non-negligible public health issue requiring some reassessment of preventive behaviors to minimize the risk of skin cancer, cataract,
and other UV-related health effects. The efforts that Mexico City has made to improve air
quality have achieved positive results in the levels of most air pollutants. Nevertheless, they
caused an increase in UV radiation that reaches the surface.

A limitation of the present work is our focus on daily maximum values, which largely exclude cloud cover. Absorption within clouds can be enhanced by the long path lengths of multiply scattered photons (e.g., Mayer et al. <sup>63</sup>), so that accurate quantification of UV effects of clouds in polluted environments remains a significant challenge and interesting opportunity for future work.

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