LETTER

Disentangling the mechanism of temperature and water vapor modulation on ozone under a warming climate

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Abstract

Temperature and water vapor have been considered as important factors affecting ozone concentrations, however, their synergistic effect on ozone, as well as its response to a warming climate remains unclear. Here, numerical experiments with different combinations of climate and emissions highlighted opposite changes of annual ozone over the contiguous U.S. under scenarios with high vs. low ozone precursor emissions in the future with warming. Comparing the occurrence of heat waves on higher vs. lower ozone days, we found significant suppression of the heat wave exacerbation of ozone by anthropogenic emissions reductions. Variations of ozone with temperature (\(T\)) and water vapor (\(Q\)) over the western U.S. and southeastern U.S. in the simulations are clearly revealed through the construction of an \(O_3\)-T-Q diagram. Based on the diagram, we further identified a \(T\)-dominant regime at higher temperatures where ozone increases with temperature increase, and a \(Q\)-dominant regime at lower temperatures where ozone decreases with temperature increase due to the negative effect of water vapor. With larger anthropogenic emission reductions, ozone may increase at a lower rate with temperature in the \(T\)-dominant regime, or even decrease with temperature in the \(Q\)-dominant regime. Our results show that with large emission reductions, substantial ozone pollution due to warming and increasing heat waves may be counteracted by water vapor, partly turning the ‘climate penalty’ on ozone into ‘climate benefit’. Hence controlling anthropogenic emissions may be an increasingly important strategy in a warmer and wetter climate to improve air quality and public health.

1. Introduction

Tropospheric ozone (\(O_3\)) has adversely affected human health via several pathways, such as increasing the risk of mortality [1, 2] and reduced crop yield [3, 4]. Tropospheric \(O_3\) is produced from complex photochemical reactions with ozone precursors (nitrogen oxides (NO\textsubscript{x}), volatile organic compounds (VOCs), and carbon monoxide (CO)) under favorable meteorological conditions [5, 6].

High temperature has been widely known as a crucial indicator of meteorological environments favorable to ozone enhancement, by strengthening photochemical reactions concomitant with strong solar radiation [7] and through the indirect effect of transport [8–10]. Consecutive days with high
temperature during heat wave events may trigger surface O$_3$ buildup [11–13] and increase mortality [14]. Under climate change, elevated overall temperatures are anticipated to enhance ozone formation, and the increased frequency, duration, and intensity of heat waves may counter the curtailment of ozone through future reductions in anthropogenic emissions [15–18]. While many studies have investigated the effect of future conditions under climate change with emissions held at the present level [18–20], given the important role of emissions and heat waves in ozone formation, understanding their linkage and interplay is vital to projecting future air quality and associated health impacts.

Although the principle effect of climate change on ozone is through warmer temperatures and thereby accelerated formation, future changes in other meteorological parameters may also play an important role in air quality. For instance, water vapor is considered one of the main sinks for tropospheric O$_3$, since water vapor may deplete the excited oxygen atom (O$^+$) and interfere with the O$_3$–O$^+$ cyclic reactions under radiation [21–23]. Through statistical analysis of historical observations, Camalier et al. [24] found that relative humidity might exert a larger negative influence on ozone than the positive influence of temperature over the southeastern U.S. With estimates that maintained ozone precursor emissions at historical levels, Collins et al. [25] and Zeng et al. [26] found large spatial variations globally in ozone responses to the meteorological impacts of climate change alone. These studies attributed the enhanced O$_3$ level to the overall temperature increase and the decrease of ozone to the elevated water vapor. The impact of water vapor on ozone depends on NO$_x$ concentration [27]. With high NO$_x$ concentration, increased water vapor may promote ozone production instead, because the chemical loss from water vapor may produce hydroxy radicals (OH) that can be converted to hydroperoxy radicals (HO$_2$) and organic peroxy radicals (RO$_2$) via reactions with VOCs and CO. Given sufficient NO$_x$ and HO$_2$, RO$_2$ could enhance O$_3$ by further oxidizing NO to NO$_2$. This mechanism was discussed in Jacob and Winner [28] to elucidate the variable sign of the response of ozone to water vapor in polluted regions. While the modulation of temperature and water vapor on ozone concentration has been discussed, how the two meteorological variables jointly constrain the ozone concentration in the future with changes in both climate and emissions has not previously been investigated.

This study aims at advancing understanding of the joint role of temperature (including heat waves) and water vapor in modulating the impacts of climate and emissions on ozone in the future. Using numerical experiments with different combinations of emissions and climate, we first isolate the impact of climate and emission changes on ozone concentration and contrast the mean ozone changes (section 3.1) with those associated specifically with heat wave events (section 3.2). These results motivate a deeper analysis of how temperature and moisture modulate the ozone response to emissions. The relationship between temperature, water vapor and ozone is addressed by introducing the O$_3$–T–Q diagram of the joint distribution of ozone as a function of temperature and water vapor (section 3.3).

2. Methodology

The impact of climate and emission changes on ozone is investigated using a regional air quality model. The same model configuration and scenarios as described in Gao et al. [17] are used in this study. The model skillfully simulates heat waves and ozone concentrations compared to observations (see Supporting Text and figures S1 and S2), and more detailed simulation results and evaluation can be found in Wang et al. [29]. Briefly, simulations from the modified Community Atmospheric Model 5.3 of the Community Earth System Model (CESM) [30, 31] are used to provide initial and boundary conditions for a regional air quality model based on WRF/Chem v3.7, for the historical period and future following RCP8.5 and RCP4.5 scenarios. The WRF/Chem simulations were performed over the continental U.S. (figure 1), with a horizontal grid spacing of 36 km and 34 vertical layers from the surface to 100 hPa. The period of 2001–2006 is considered the historical period. Though the warming signal may be stronger in the far future, e.g., by the end of the century, the anthropogenic emission projections could suffer larger uncertainties beyond mid-century, therefore, the mid-century period of 2046–2055 is used as the future period. Nevertheless, the findings in this study should hold over the far future as well. The projection of anthropogenic emissions in simulations is driven by scenarios generated by the technology driver model (TDM), which is updated based on the Intergovernmental Panel on Climate Change A1B and B2 scenarios, by taking into account technological development, including in the transportation, industry, power plants and residential sectors [32, 33]. The comparison in ozone precursor emissions between TDM A1B/B2 and RCP 8.5/4.5 is shown in figure S3, indicating that TDM A1B/B2 owns similar NO$_x$ emission and higher non-methane volatile organic compound (NMVOCs) emissions compared to RCP 8.5/4.5. Compared to TDM B2, TDM A1B features a larger increase in greenhouse gas emissions but lower reduction in air pollutant emissions [31, 32]. For simplicity, the A1B and B2 scenarios used below refer to the TDM A1B and TDM B2 scenarios. The biogenic emissions are generated online by the Model of Emissions of Gases and Aerosols from Nature (MEGAN) version 2 [34].

The WRF/Chem simulations during the historical period are referred to as Hist, and the simulations
for the future period with changes in both climate and emissions following the A1B and B2 scenarios are called $E_{A1B}M_{A1B}$ and $E_{B2}M_{B2}$, where $E$ and $M$ refer to emission and meteorology, respectively. Sensitivity experiments are also performed, in which all anthropogenic emissions in the future are the same as A1B or B2, but the meteorological conditions follow those of the historical conditions (i.e. WRF/Chem driven by the same meteorological boundary conditions of the CESM historical simulation). These simulations are called $E_{A1B}M_{his}$ and $E_{B2}M_{his}$, respectively. Despite the cloud-aerosol-meteorology feedback in WRF/Chem, meteorological conditions are comparable between the historical and the sensitivity experiments ($E_{A1B}M_{his}$ and $E_{B2}M_{his}$) over most of the contiguous U.S., e.g., the six year mean differences over the contiguous U.S. (CONUS) are within 0.2 °C for 2 m air temperature, 0.1 m s$^{-1}$ for wind speed at 10 m, 0.3 mm d$^{-1}$ for daily total precipitation, and 0.2 g kg$^{-1}$ for daily mean water vapor. Therefore, comparison between the Hist and the sensitivity experiments can be used to isolate the impact of emissions (A1B and B2) and climate.

3. Results

3.1. Impact of climate and emission changes on ozone concentration

Figure 1 shows the difference of annual mean maximum daily 8 h average (MDA8) ozone concentration, comparing the historical simulation (Hist) with the future simulations under the A1B and B2 scenarios. With higher greenhouse gas emissions, A1B features warmer surface temperatures compared to B2 (figure S4), although the future temperature changes are statistically significant ($t$-test, $\alpha = 0.05$) for both A1B and B2. To establish the robustness of the temperature change relative to internal variability, we compare the temperature changes due to external forcing (figure S5(a)) and the standard deviation of temperature across 35 members of the CESM1 Large Ensemble Simulations under RCP 8.5 [35] (figures S5(b)–(d)). Whereas the results or findings are sensitive to internal variability [36], the results indicate that the temperature changes due to internal variability (figures S5(b)–(d)) are, in general, much smaller than those due to the external forcing (figure S5(a)).

The projected changes of ozone mid-century (figures 1(a) and (d)) for the A1B and B2 scenarios differ in both sign and magnitude. For quantitative comparison, average values over CONUS, western U.S. (WUS) and southeastern U.S. (SEUS) are provided at the top of each panel. Ozone decreases throughout CONUS under B2, but increases in most of the U.S., except for parts of SEUS under A1B. The contrast between the two scenarios can be understood by decomposing them into the impacts of emission changes (figures 1(b) and (e)) and climate change (figures 1(c) and (f)).
With the same meteorology as Hist (figures 1(b) and (e)), the reduction in emissions in the future generally yields a mean decrease of ozone concentration by 2.1 ppbv and 2.8 ppbv under A1B and B2, respectively, over CONUS, with larger reductions of ozone in B2 consistent with the larger emissions reductions in B2 compared to A1B. In both scenarios, the emission reductions in SEUS are larger than those in WUS, leading to more intensified ozone decreases in this region. A detailed delineation of the seasonal variability (figures S6–S9) shows consistent features with those of the annual mean, except in winter, when the photochemistry is weak and titration plays a dominant role, so the reduction in NOx may induce ozone increase over large areas (figures S9(b) and (e)), supported by a previous study (i.e., figures S3(a)–(d) in Gao et al [12]).

With the same projected emissions in the future under the A1B or B2 scenarios, comparison of the simulations with future and historical climates helps isolate the effect of meteorological changes. The average influence on ozone over CONUS from climate change alone is 3.4 ppbv and −1.3 ppbv under A1B and B2 (figures 1(c) and (f)), respectively. Therefore, the positive change in ozone in A1B (figure 1(a)) is primarily induced by the increase in ozone with climate change (figure 1(c)). The sign difference in annual mean ozone between A1B and B2 is consistent with the seasonal scale depicted in figures S6–S9, with the exception of summer when climate effect alone in the future may facilitate ozone formation and induce an increase in ozone concentration, even under the B2 scenario (figures S6(c) and (f)). Whereas it is expected that a warming climate in the future leads to a mean increase of ozone under A1B (figure 1(c)), it may seem counter-intuitive that warming in B2 results in a decrease of ozone in large areas of the U.S. (figure 1(f)). Before investigating the detailed mechanisms for the reductions in ozone with warming under the B2 scenario (section 3.3), the heat waves contributions to the ozone changes under various scenarios are analyzed in the next section to further evaluate the relative impacts of climate and emission changes on ozone during heat waves.

3.2. Impacts of heat waves on ozone

To examine the impact of heat waves on ozone, the spatial distributions of changes in ozone concentrations in the future due to the combined effect of climate and emissions (figures 2(a) and (b)) and climate change alone (figures 2(c) and (d)) are examined. There is no standard definition of a heat wave in science or policy, but a heat wave is commonly defined by duration and intensity. Here, we define a heat wave as an event with at least three continuous days with a daily maximum temperature at 2 m (MaxT2) exceeding the threshold defined by the 97.5th percentile of Hist, and the same threshold is used in both historical and future periods, following the definition in a previous study [37].

Ozone concentrations formed under heat waves generally decrease due to the combined effect of climate and emissions by 7.4 ppbv under $E_{A1B}M_{A1B}$ and −10.3 ppbv under $E_{B2}M_{B2}$ over CONUS. These reductions are much larger compared to the mean changes shown in figure 1, supporting the idea that ozone changes are amplified during heat waves. The decrease is largely induced by the reduction in emissions, as inferred from the increase or no change in ozone due to climate change alone (figures 2(c) and (d)).

It is noteworthy that the signs of ozone changes due to climate change alone (figures 2(c) vs. (d)) are generally consistent in SEUS between A1B and B2, but different over WUS, with the underlying mechanism discussed below. The probability density functions (PDFs) of MDA8 ozone concentration over these two regions are displayed in figures 2(e) and (f). The opposite changes over WUS are clearly depicted by the opposite shifts of the PDFs between the present and future under the two scenarios. Over SEUS, a clear right shift is discernable under A1B (blue line vs. green line in figure 2(f)), but the PDFs for the present and future climate are almost indistinguishable under B2 (orange line vs. red line in figure 2(f)). Despite these differences in the change of the PDFs, the mean ozone enhancement between the two scenarios is comparable in SEUS (1.3 ppbv and 1.0 ppbv in figures 2(c) and (d)).

To visualize the impact of heat waves on the concentrations of MDA8 ozone, the ozone concentrations on days identified as heat waves are marked in a different color on each PDF curve. As temperature is closely linked to ozone formation, we expect heat waves to be identified more frequently on the right side of the peak of the PDF with higher ozone concentration than on the left side. To evaluate the extent to which heat wave events modulate the ozone pollution, we calculate the ratio of the total number of heat wave days identified on the right side of the peak of the PDF to that on the left side. This ratio, representing the degree of the heat wave modulation on ozone, has values of 3.7 and 15.0 over WUS and SEUS, respectively, for the historical simulation, indicating that for regions with high emissions (SEUS), the occurrence of heat waves predominantly coincides with high ozone days. With emission reductions under A1B and B2 but the same present-day climate, the ratio tends to become smaller even with the same meteorological conditions, with values of 1.9 and 7.3 for WUS and SEUS, respectively, under the A1B emission scenario (green lines in
Figure 2. Impacts of climate change and emissions on MDA8 ozone under heat wave. (a)–(d) display the spatial distribution of ozone response to climate change and emission, showing only values passing the t-test ($\alpha = 0.05$), and the numbers provided at the top have the same meaning as those in figures 1(e) and (f) that display the probability density functions (PDF) of ozone over western and southeastern U.S. Each bin of the PDF is 3 ppbv, and within each bin, the days identified as heat waves are marked by white blocks. Considering that the number of heat waves in some bins could be very small, the length of the heat wave blocks is multiplied by a factor listed on the top left. The ratio of heat wave days on the right side of each PDF to the left side is listed as well on the bottom for comparison.

figures 2(e) and (f)). These ratios become even smaller (1.3 for WUS and 4.7 for SEUS) with larger emissions reductions in B2 (red lines in figures 2(e) and (f)). These results indicate that emission reductions significantly reduce the impact of heat waves on ozone under the present-day meteorological conditions.
In the future with warming, the frequency of heat waves increases. However, the degree of the heat wave modulation on ozone may change to alter the ratio of the number of heat wave days on the right and left sides of the ozone PDF. Based on the simulations, the ratio is reduced over SEUS where emissions is relatively larger than WUS. This is particularly apparent for the A1B scenario, with a ratio of only 1.7 in the future, indicating the largest decrease due to climate change (compared to 7.3 under A1B with present-day meteorology). The redistribution of heat wave days on the two sides of the PDF partly explains the mixed increase and decrease of MDA8 ozone in SEUS (figure 2(d)). These results, comparing simulations with present and future climate and between emission scenarios with different levels of emissions reductions, strongly imply that the modulation of heat waves on ozone concentration is constrained by emissions. The latter is also supported by the much smaller ratio over WUS than SEUS with different emissions levels.

Considering the ozone standard of 70 ppbv for the MDA8 ozone [38] with harmful effects on human populations, the likelihoods of ozone exceedance in all days and under heat waves are listed in table S1 for all the scenarios. The increase of the likelihood under heat waves compared to all days, reflecting the modulation of ozone exceedance by heat waves, shows strong positive correlation with emissions across different scenarios and regions. The increase vanished in WUS under the B2 scenario featuring the lowest emissions. This implies that reducing emissions to certain levels could eliminate the impact of heat waves on ozone exceedance, which is particularly useful for ozone pollution control during heat waves, similar to the concept of dynamic emission control proposed by Yan et al [39]. The additional benefit of emission reductions in reducing not only mean ozone concentrations but also high ozone episodes during heat waves is also supported by figure S10, showing that heat wave effect is significantly reduced with emissions reductions.

Considering the bias in simulations of heat waves (figure S1), the relationship between heat waves and ozone mentioned above may encounter uncertainties. To estimate to what extent heat wave days may affect the relationship, a range of tests is designed through perturbing the original threshold at an interval of 0.02 °C in both directions, and the perturbation ends when changes in mean heat wave days over CONUS due to threshold perturbations approach the value of mean fractional error (MFE) (28% in this case). The amplification effect of heat waves on ozone and ratios of heat wave days associated with higher vs. lower ozone concentrations (table S2) support the discussions above, further stressing the vital role of emission in constraining the heat wave effect on ozone.

3.3. Effect of temperature and water vapor on ozone

From figure 1 (figures 1(c) vs. (f)), future warming and emissions reduce ozone concentration under the B2 emission scenario, which is in stark contrast to the increased ozone under the A1B scenario. Besides the larger suppression of the modulation of heat waves on ozone under B2 with larger emissions reductions than A1B, the contrasting impact may be associated with differences in temperature and water vapor changes under the two scenarios. In particular, the ozone reduction in B2 could be due to increased water vapor acting as the main sink of tropospheric O₃. Previous studies have implicated the dual effect of water vapor on ozone, by acting either as a sink leading to decreases of ozone, or as a source triggering the increase of ozone [27]. While studies in the past investigated the impact of temperature and water vapor separately [24, 40], water vapor is positively correlated with temperature based on the Clausius–Clapeyron equation, i.e. ~7% increase of water vapor for 1 °C rise of air temperature, with generally small changes in relative humidity [41]. Therefore, water vapor is expected to increase under a warming climate, leading to a possible competition between temperature and water vapor in modulating the ozone concentration.

To investigate the response of ozone to temperature and water vapor simultaneously, we construct the two-dimensional distribution of ozone as a function of near surface air temperature (T) and water vapor (Q) in the historical simulation (figure 3). The joint PDF (figures 3(a) and (b)) shown for WUS and SEUS reveals a few striking features: water vapor generally increases with temperature, except for the right tail, which is mainly attributable to the reduced sample size. While the range of temperature is similar between the two regions, SEUS has a more frequent occurrence of higher water vapor compared to WUS. This reflects the more humid conditions in SEUS and the semi-arid conditions in WUS due to atmospheric circulation differences. Over WUS, there is a high concentration of areas with lower temperature and lower water vapor and the distribution is more dispersed, suggesting a weaker relationship between temperature and water vapor in the semi-arid region. In contrast, the narrow banded structure of the PDF in SEUS indicates a stronger relationship between temperature and water vapor, suggesting a larger contribution of local evaporation to water vapor in this region.

In terms of the ozone response to T and Q, the effect is, in general, positive for temperature but negative for water vapor in the O₃-T-Q diagrams developed to reveal the dominant meteorological factors modulating the ozone concentration, to facilitate understanding of the underlying mechanism
Figure 3. Ozone distribution as a function of the daily maximum temperature ($T$) and daily mean water vapor ($Q$). (a) and (b) show the two-dimensional probability density distribution of data points for $T$ and $Q$ over the western U.S. and southeastern U.S., while the red lines depict the variation of composited water vapor with temperature. Only $T$-$Q$ bins with sample size higher than 20 are shown in color. (c) and (d) show the average ozone concentration in each valid $T$-$Q$ bin corresponding to (a) and (b). The inset line charts ($c_1$, $c_2$, $d_1$, $d_2$) show ozone concentration with composited (black) and fixed (pink) water vapor and temperature values. Ozone contours are fitted using transformed sigmoid functions with the formula provided at the top while $k$, $a$, $b$ and $c$ are fitting parameter variables by line. Please note that temperature and water vapor are rescaled to 0–1 using min–max normalization before fitting and remarked as $T_{\text{Normalized}}$ and $Q_{\text{Normalized}}$. The vertical dashed lines define different regimes indicating the dominance of ozone variation by $T$ and $Q$ with increasing temperature.

of ozone changes (figures 3(c) and (d)). The $O_3$-$T$-$Q$ diagrams adapted the widely-used empirical kinetic modeling approach diagrams to display the relationships between $O_3$ and its precursors (VOCs and NO$_x$). To determine the best fit for the relationships between $O_3$ and $T$ and $Q$, three different functional forms were tested including polynomial, exponential and transformed sigmoid functions, with the latter yielding the best fit in terms of the minimal residual sum of squares. The formula of the sigmoid function is listed at the top of figures 3(c) and (d) highlighted in yellow. While the sigmoid function tends to flatten at very high temperature, the polynomial or exponential function may increase indefinitely, so the sigmoid function is closer to the ozone response determined by the model.

On average, ozone increases with temperature but decreases with water vapor, as shown by the pink lines in figures 3($c_1$), ($c_2$) and ($d_1$), ($d_2$) delineating the relationship between ozone with temperature or water vapor with the other variable fixed at a certain level. In SEUS, ozone increases more rapidly with temperature (figure 3($d_1$)) but decreases at a lower rate with water vapor (figure 3($d_2$)) compared to WUS (figures 3($c_1$) and ($c_2$)). The contrasting relationships between the two regions are attributable to
the difference in emissions, as the relationships are compared within similar ranges of temperature and water vapor between the two regions.

It should be noted that the O₃−T−Q relationship does not work well over SEUS for temperature higher than 30 °C (figure 3(d)). While previous studies generally highlighted the importance of sufficient NOₓ emissions for the positive water vapor effect, co-occurrence of high temperature may be important, because water vapor affects ozone mainly through the photochemical chain reaction, which is enhanced by warmer temperature. Since the negative effect of water vapor works directly through reaction with H₂O to reduce O₃ production in the O₃−O [¹D] cycle, the chain reaction modulating the negative effect operates on a much shorter timescale than that modulating the positive effect, so water vapor would be first consumed to produce a negative effect, which suppresses the positive effect by depleting the water vapor needed. The phenomenon that ozone concentration first decreases and then increases with increasing water vapor can be seen by comparing the shading before and after a certain high temperature point such as 35 °C in SEUS (figure 3(d)), indicating the positive water vapor effect could become dominant under high temperatures and emissions.

Considering the competition between temperature and water vapor in the ozone concentration response, the O₃−T−Q diagram shows a possible transition zone separating the dominance of temperature vs. water vapor. This is demonstrated by the water vapor weighted response of ozone to temperature displayed by the black curve in figure 3(c₁), with each point on the curve representing the mean ozone (figure 3(c)) weighted by the respective sample size (figure 3(a)) for each temperature bin. The curve delineates a three-segment characteristic, where ozone decreases first with the increase of temperature, followed by a segment with near constant ozone, and then an increase with the temperature. The variation of ozone concentration with temperature reflects the effect of both temperature and water vapor. In fact, a similar phenomenon is discernable in figure 3 of Camaleri et al [24], which focused however, on the right tail with high temperature, ignoring the counterintuitive negative effect when temperature is low. The latter is clearly revealed by the O₃−T−Q diagram. Please note that during the period with higher temperature, e.g., the season of summer, temperature tends to play an important role as well as downward surface solar radiation, considering that heat waves are often concomitant with solar radiation [42]. However, in the colder period, e.g., the season of fall, downward surface solar radiation may play an even larger role than temperature [43], stressing a potentially joint control of solar radiation and water vapor on ozone, which deserves future investigation.

To better quantify the points defining the transition zone, we apply an 11-point moving average along the black curve (figures 3(c₁) and (d₁)) and calculate the ozone differences between adjacent points on the smoothed curve starting from the left. The transition zone is defined by the widest temperature range covering all contiguous points with absolute adjacent differences less than the standard error (standard deviation divided by the sample size) within the −10 °C–25 °C range with sufficient sample size, shown as the grey dashed lines in figures 3(c) and (d). Within the transition zone, the impact of T and Q on ozone nearly cancel each other out, resulting in minor changes in ozone. The left side of the transition zone is a Q-dominant regime while the T-dominant regime is on the right. In SEUS, concomitant with the larger slope variation reflected in the O₃−T−Q diagram, the transition zone (2.9 °C–6.9 °C) is narrower than that in WUS (3.2 °C–18.8 °C), although the starting temperature of the transition zone is comparable between the two regions. The difference in the width of the transition zone implies that in SEUS with higher emissions, there is a larger range of temperatures for which the temperature effect on ozone dominates over the water vapor effect, while in WUS with lower emissions, water vapor plays a larger role, as low emissions may weaken the promoting effect of water vapor and the temperature effect simultaneously.

Analysis of the O₃−T−Q diagrams for the future scenarios (figure S11) and sensitivity experiments (figure S12) shows that the O₃−T−Q relationship discussed for the historical simulation (figures 3(c) and (d)) generally holds for all scenarios. However, concomitant with the emissions reductions, the isolines of ozone concentration in both sensitivity experiments and future scenarios tend to flatten along with minor differences within themselves, implicative of a larger role of water vapor and the weakened effect of temperature.

To more clearly demonstrate the role of emissions in modulating the O₃−T−Q diagram, the dependence of ozone on temperature integrated over the water vapor values from the historical simulation (black curves in figures 3(c₁) and (d₁)) is shown along with the corresponding curves for the sensitivity experiments (figures 4(a) and (b)). A striking contrasting feature is noted: in the T-dominant regime, ozone increases with temperature at a much lower rate in the sensitivity experiments (with reduced emissions) than the historical simulation over both WUS and SEUS. As a result, ozone concentration is much lower in the future scenarios than that in the historical simulation when temperature is higher than ~20 °C. Moreover, the rate at which ozone increases with temperature is lower in B2 (with larger emissions reductions) than A1B scenarios. The contrast between the sensitivity experiments and historical simulation and
Figure 4. Ozone concentration with composited water vapor (the same as the black lines in figures 3(c) and (d)) in both historical and sensitivity experiments, along with the corresponding definition of regimes dominated by $T$ and $Q$.

Figure 5. A schematic diagram for the modulation of ozone by temperature ($T$), water vapor ($Q$) and emissions of ozone precursors ($E$). The left panel demonstrates the mechanism of how $T$, $Q$ and $E$ affect ozone modulation, and the right panel illustrate the relative relationships between $T$, $Q$ and $E$. The grey dashed line marks the transition between the $T$-dominant and $Q$-dominant regimes as a function of emissions. Historical, future and sensitivity scenarios are marked by the grey points, while the ozone difference among the scenarios are labeled by (increase) and (decrease).

between B2 and A1B is larger over SEUS (with larger reductions in emissions in the scenarios) than WUS.

It is interesting to note that at the lower temperature range of the $T$-dominant regime in SEUS, ozone concentration is higher in the sensitivity experiments than the historical simulation, suggesting a negative relationship between ozone and emissions at lower temperatures. This contrasting behavior compared to the higher temperature range may be due to the weakened NO titration effect, as ozone production is limited at the lower temperature range, leading to a slightly diminished transition zone in the sensitivity experiments. For WUS, with low historical emissions and small reductions level in A1B and B2, the lines lying in the $Q$-dominant regime are nearly the same between the sensitivity experiments and historical simulation, as there is almost no interference by NO titration. Under this circumstance, the transition zone is widened owing to the weakened temperature effect. Overall, analysis of the $T$-dominant regime across regions and scenarios with contrasting emission reductions supports the important role of emissions in the temperature control on ozone.

The mechanism of ozone response to temperature, water vapor and emissions are summarized schematically in figure 5, which first visualize these impacts, and then depicts a Cartesian coordinate with the $x$-axis denoting emissions and the $y$-axis denoting meteorology, mainly including temperature and water vapor. The ozone response to emissions and the meteorological parameters under different scenarios are represented in the coordinate system. Moreover, we simplify the separation between the $T$-dominant regime (red area) and the $Q$-dominant regime (blue area) by the dashed grey curve. Given high enough emissions, such as in the present-day, the temperature at which the transition to the $T$-dominant regime occurs is less sensitive to the emissions, so the dashed grey curve flattens at the right. Warming beyond this curve could lead to ozone increase (such as A1B, representing climate penalty) while warming under the transition curve (blue area) could lead to ozone reduction (such as B2, representing climate benefit).

4. Discussions and conclusions

Using numerical experiments featuring a combination of simulations with historical vs. future (warmer) climate and current vs. future (reduced) emissions, the impact of climate change and anthropogenic
emissions changes on ozone concentration is investigated. While warming in the future generally favors higher ozone concentration, we found opposite changes of annual ozone under the A1B and B2 scenarios in the future, with ozone enhanced in A1B but reduced in B2. This finding motivated deeper analyses of the role of warming and emissions on annual ozone and ozone exceedance. Using the ratio of the number of heat wave days associated with higher vs. lower ozone concentrations as a metric, we found consistent reduction in this ratio in all future scenarios relative to the historical simulation and larger reduction in the southeastern U.S. with higher emissions than in the western U.S. with lower emissions. These results imply that the efficacy of heat waves in inducing high ozone is significantly constrained by emissions reductions and the modulation of heat waves on ozone pollution episodes can even be completely eliminated by larger reductions such as featured in the B1 scenario.

As temperature and water vapor are closely related through the Clausius–Clapeyron equation, understanding the ozone response to climate and emissions changes requires a more systematic analysis of the joint dependence of ozone on temperature and water vapor. Constructing an $O_3$-$T$-$Q$ diagram to display the variations of ozone as a function of $T$ and $Q$, we identified the seesaw effect of temperature and water vapor in modulating the ozone concentration. In particular, temperature plays a predominantly positive role, except at lower temperatures where the negative role of water vapor overwhelms the positive effect of temperature. This behavior can be described by the $T$-dominant regime at higher temperatures where ozone increases with temperature, and the $Q$-dominant regime at lower temperatures where ozone decreases with temperature due to the negative water vapor effect, with the two regimes separated by a transition zone. Comparing the future scenarios with the historical simulation shows a robust decrease in the rate at which ozone increases with temperature in the $T$-dominant regime, attributable to the emissions reductions in the future scenarios.

Figure 5 schematically summarizes the control of emissions and meteorology on ozone and explains the increase in annual ozone under the A1B scenario, where ozone concentration increases with temperature in the $T$-dominant regime, in contrast with the decrease in annual ozone under the B2 scenario, where ozone concentration decreases with temperature in the $Q$-dominant regime. The distinct and opposite ozone responses in the A1B and B2 scenarios are marked by the larger emissions reductions, and hence reduced warming, in B2 relative to A1B. The ozone response could be rather sensitive to the scenarios and climate models used in projecting future ozone changes. Besides the dependence of the ozone precursor emission reductions on the socio-economic scenarios, the warming response is sensitive to both the emissions and the climate models, and the transition zone between the $T$-dominant and $Q$-dominant regime and the heat wave modulation on ozone may also be sensitive to the climate models and their representations of ozone chemistry. Although this study analyzed results based on simulations by a single model driven by two specific emissions scenarios, it has advanced a conceptual framework to understand the ozone response to emissions and climate changes and underscored the mechanistic relationships (the $O_3$-$T$-$Q$ diagram and the metric of heat wave modulation on ozone) that can be derived using observations to constrain climate models and their projections of future ozone changes.

In summary, this study highlights the important role of anthropogenic emissions in the modulation of the temperature and water vapor effect on ozone, which explains the opposite response of ozone between the A1B and B2 future scenarios. This modulation by emissions is particularly significant at higher temperatures, such as during heat waves that exacerbate ozone. It is noteworthy that methane is likely to play a more important role in affecting ozone concentrations under the decrease of major anthropogenic emissions, and the specific effect deserves further investigation in future. Therefore, emissions reductions will be increasingly important in a warmer and wetter climate as a strategy to avoid air pollution episodes and reduce the associated public health risk.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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