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IDEALIZED PARTICLE-RESOLVED LARGE-EDDY SIMULATIONS
TO EVALUATE THE IMPACT OF EMISSIONS SPATIAL HETEROGENEITY
ON CCN ACTIVITY

BY

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THESIS

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Abstract

Aerosol-cloud interactions remain a large source of uncertainty in climate models due to complex, nonlinear processes that alter aerosol properties and the inability to represent the full compositional complexity of aerosol populations within large-scale modeling frameworks. The spatial resolution of these models (typically 10-100 km) is often coarser than the spatially varying emissions in the modeled geographic region. This results in diffuse, uniform emission of primary aerosol and gas-phase species instead of spatially heterogeneous concentrations. Aerosol processes such as gas-particle partitioning and coagulation are concentration-dependent, and thus the representation of spatially heterogeneous emissions impacts aerosol aging and properties. This includes climate-relevant quantities like particle hygroscopicity and cloud condensation nuclei (CCN) activity.

This thesis investigates the impact of emissions spatial heterogeneity on CCN activity by using the particle-resolved model PartMC coupled to the Weather Research and Forecasting model configured for large-eddy simulations (LES). The resulting modeling framework resolves turbulence-chemistry interactions and aerosol aging on a per-particle scale. The sensitivity of CCN activity to emissions spatial heterogeneity is evaluated for primary aerosol and gas-phase emissions typical of urban regions. The pattern of emissions is varied to investigate a range of spatial heterogeneity scenarios. For each scenario, CCN activity is compared against a uniform emissions base case to determine the impact of spatially heterogeneous emissions.

TODO: update! We find that CCN concentrations decrease by as much as 10% with increasing emissions spatial heterogeneity, especially for low supersaturations ($S=0.1, 0.3\%$). This work is a first of a kind application of high resolution, particle-resolved LES for quantifying structural uncertainty of CCN activity due to the representation of emissions spatial heterogeneity.

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Chapter 1

Introduction

This chapter discusses fundamental properties of aerosols and computational modeling techniques which motivate this thesis. A description of atmospheric aerosols and the challenges associated with capturing the complexity of aerosol properties and their environmental feedbacks is discussed. Additionally, numerical modeling treatments for aerosols are presented along with approaches to improve the characterization of aerosol complexity. Finally, research questions are presented which outline primary avenues of inquiry for this thesis.

1.1 The complexity of aerosols and environmental feedbacks

An aerosol is a collection of particles composed of one or more chemical species that are suspended in a fluid or gas. In the atmosphere, aerosol particles vary considerably in terms of their physical properties such as size, composition, and origin. Additionally, the chemical, thermodynamic, and radiative properties of aerosol particles can alter the state of the aerosol and the surrounding environment through numerous feedback mechanisms. In turn, aerosol particles exhibit a complex, non-linear coupling with the environment that spans broad spatial and temporal scales.

Aerosol particles are typically measured by their diameter where spherical morphology is assumed. The smallest particles have diameters on the order of 1 nm and are produced via the nucleation of low-volatility vapors. On the opposite extreme of particle sizes, the largest particle diameters can exceed 100 μm . In total, aerosols span approximately five orders of magnitude. To capture the broad scale of particle diameters that may be present in a population of aerosol particles, aerosol size distributions often represent the number concentration of particles as a function of the logarithm of particle diameter. The particle size distribution may be represented by multiple modes—lognormal size distributions—that are differentiated by the characteristics of particles within each mode, including growth and removal mechanisms. Typically, three distinct modes are

present in a particle size distribution: the nucleation, accumulation, and coarse mode.

Nucleation mode particles are up to 20 nm in diameter and undergo rapid growth as gas-phase species condense onto the particle surface or as particles inelastically collide through coagulation. They are removed from the nucleation mode by growth within XX time into the accumulation mode, which spans particle diameters from 0.1 μm to 2 μm . In addition to particles that enter the accumulation mode through growth by condensation or coagulation, particles may be released directly into the accumulation mode via primary emissions. Removal mechanisms such as wet and dry deposition are least efficient in the accumulation mode, allowing particles to remain suspended in the atmosphere for days to weeks. Particles in the coarse mode have diameters exceeding 2 μm and are produced by mechanical processes such as abrasion and the resuspension of dust. Due to their size, particles in the coarse mode are rapidly removed by gravitational settling within minutes to hours. This multi-modal description of the aerosol size distribution points to the inherent complexity of aerosol population dynamics—production, growth, and removal mechanisms differ considerably by particle size.

As noted, production mechanisms vary across aerosol modes (e.g., nucleation of low-volatility vapors, emission of primary aerosol into the accumulation mode, resuspension of coarse particles, etc.). These processes typically involve different chemical species. For example, whereas volatile organic compounds (VOCs) such as isoprene and other organic carbon (OC) species may undergo oxidation reactions which lower their volatility and promote particle nucleation, particles released directly into the accumulation or coarse mode as primary aerosol may consist of either organics that are produced during combustion such as black carbon (BC) or inorganics such as sea salt spray, mineral dust, [other species]. Here its worth acknowledging contribution of precursor emissions to chemical aging, secondary production of aerosol-phase matter, changes to aerosol mixing state, etc.. As a result, aerosol particles are compositionally diverse.

In addition to diversity in the composition of aerosol particles across the size distribution, aerosol populations also exhibit spatiotemporal variations which alter the local structure and composition of the aerosol. The geographic distribution of emission sources, varied land use, and topography lead to spatial heterogeneities in the emission of gas-phase precursors and primary aerosols. Additionally, temporal trends alter the meteorological state of the atmosphere and the concentration of reactive gas or aerosol-phase species. For instance, diurnal variation in the structure of the boundary layer due to surface heating determines the strength of vertical transport and mixing of primary aerosol or reactive gas-phase species. [Could talk about photolysis]. Furthermore, the timing of emissions may play a crucial role in determining whether a chemical

reaction will take place; reactive species must be present in the same space and time to undergo reaction.

Seinfeld and Pandis [1998](#)

1.2 Spatial heterogeneity of aerosols

- Spatial heterogeneity of surface heterogeneities impacts the evolution of the atmospheric state
 - Joint modeling and observation based studies like Fast et al. 2019 “HI-SCALE” heterogeneities in soil moisture were critical to cloud structure and the development of deeper convecting clouds. Modeling studies showed that under scenarios with smoothly varying soil moisture, clouds did not develop into open cell, deep convective cumulus capable of precipitating and instead were characterized by shallow, uniform non-precipitating clouds.
 - Lee et al. 2018 conducted an idealized LES study in which surface heat fluxes (including both sensible and latent heat flux) were prescribed by checkerboard patterns of ranging spatial heterogeneity (most heterogeneous being the lowest frequency checkerboard pattern—largest pattern length scale—and least heterogeneous being the highest frequency patterns—smallest pattern length scale). They found that secondary circulation developed under scenarios with the highest spatial heterogeneity and minimal background winds (less than 2 m s^{-1}). This circulation was responsible for transporting moisture from checkerboard regions with greater latent heat flux to drier regions with lesser latent heat flux.
- Aerosols have shown to also be highly variable:
 - Examples: Urban, rural, maritime, etc. (variability in composition, concentration). See Seinfeld and Pandis for some discussion of typical conditions in each region.
- Existing studies looking at spatial heterogeneity of aerosols
 - Fast et al. 2022 (properties)
 - Hassan et al. 2023 (emissions)
 - Franklin et al. 2018
- Impacts on aerosol processes: non-linear, concentration dependent processes

- Coagulation
- Chemistry
 - * Present body of literature investigates predominantly gas-phase chemistry (e.g., isoprene-OH reaction) and contribution of chemical segregation due to turbulence and spatial distribution of reactive species
 - These processes alter the radiative and hygroscopic properties of the aerosol
- Representation of aerosol spatial heterogeneity in models
 - Lack of resolution, impact of sub-grid scale variability on aerosol properties (Radiative properties, CCN concentrations)
 - * Lin et al. 2017 find that aerosol (mass I think) SGV over the pacific ocean within a typical GCM grid cell is 15% near the surface and as high as 50% in the free troposphere. (this could also be cited in the paragraph above on variability of aerosols).
 - * Weigum et al. 2016 look at the effect of SGV on AOD and CCN by comparing WRF-Chem runs at 80 km resolution against 10 km resolution and find an underestimation of AOD by 13% and an overestimation of CCN by 27%. They find gas-phase chemistry and aerosol water uptake are processes which are most affected.
 - * Qian et al. 2010 (study over mexico, contribution of emissions to SGV)
 - * Gustafason et al. 2011 (similar to Qian 2010, radiative effects)
 - * Crippa et al. 2017
 - Attempts at parameterizations (adaptive grids, plume in grid modeling, coagulation parameterizations, PDF-based methods, stochastic fields, etc.)

1.3 Impacts of aerosols on climate

- Aerosol-radiative effects
 - Absorption and scattering of radiation alters the stability of the atmosphere due to warming/cooling

- Aerosols alter large scale circulation. For example, higher aerosol concentrations due to anthropogenic activity in the northern hemisphere results in global-scale heterogeneity. Fan et al. 2016 (via Ming and Ramaswamy 2011) note that this weakens the northern branch of the Hadley circulation, resulting in an energy flux from the southern hemisphere towards the north.
- Aerosol-cloud interactions
 - Indirect effects - Twomey, etc.
 - Impacts on cloud type and evolution
 - * Warm rain mechanism well understood
 - * Thermodynamic invigoration due to increased CCN for deep-convective clouds (mechanism much more complicated, still contested)
 - * Have been shown to promote formation of open cells
 - Radiative forcing due to ACI and sources of uncertainty
 - * One source of uncertainty is aerosol representation in models

1.4 Treatment of aerosols across modeling frameworks

- Simplified bulk, modal, sectional treatments
 - Use in regional, global scale models
 - Consequences of simplified treatment on representation of CCN concentrations, etc.
- Particle resolved aerosol modeling
- Transport representation
 - Large scale models use RANS and thus cannot resolve turbulence and associated heterogeneities in gas, aerosol concentrations
 - LES - adoption for modeling aerosols is still nascent, some examples like UCLALES-SALSA, DALES have been used to evaluate aerosol-cloud interactions, but none leverage a high-resolution particle resolved aerosol treatment

1.5 Objectives of this thesis

- Primary science questions
 - Impacts of emissions spatial heterogeneity on aerosol processes (e.g., coagulation, chemistry, etc.)?
 - Impacts of emissions spatial heterogeneity on aerosol properties (e.g., composition, concentration, hygroscopicity)?
 - How is the impact of spatial heterogeneity on aerosols modulated by changes to the composition of emissions?
 - How does emissions spatial heterogeneity alter the activity of CCN?
- Development of a framework for evaluating spatial heterogeneity impact on aerosol properties, including CCN activity
 - Transport vs. aerosol treatment graph
 - Future extension could quantify the structural uncertainty for the representation of aerosols (properties, ccn activity, etc.) in coarser resolved models such as regional and global scale models that use modal/sectional aerosol treatments and parameterize turbulence

Col1	Col2	Col2	Col3
1	6	87837	787
2	7	78	5415
3	545	778	7507
4	545	18744	7560
5	88	788	6344

Table 1.1: Table to test captions and labels.

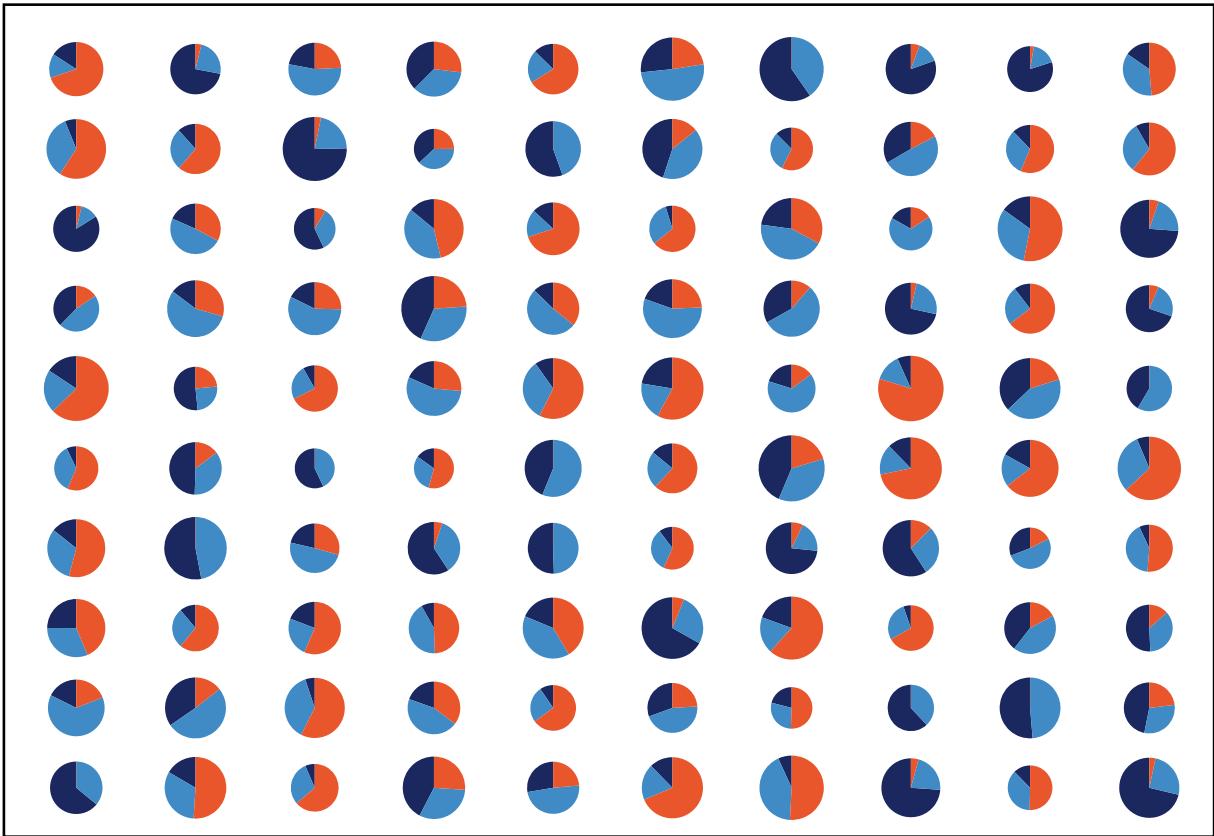


Figure 1.1: Cartoon representation of a particle resolved model

Chapter 2

Quantifying emissions spatial heterogeneity and mixing

This chapter provides an overview of spatial heterogeneity (SH) and its relevance to quantifying the spatial variability of atmospheric emissions. We begin with a brief discussion of cross-disciplinary efforts to quantify SH. We then narrow our focus to quantifying the heterogeneity and mixing of reactive compounds in the atmosphere and characterize the gap in existing approaches that necessitate the development of a new, generally applicable SH metric that we will use in this thesis. The remainder of this chapter is dedicated to discussing our novel SH metric, the development of a Monte-Carlo based method for efficiently computing the metric over large domains, and its application to measuring the SH of idealized 2D patterns.

2.1 Existing Approaches to Quantifying Spatial Heterogeneity

SH is ubiquitous across the natural sciences ranging from ecology to atmospheric sciences. SH plays an important role in biological diversity, human land use and associated environmental feedbacks, and drives changes in atmospheric dynamics through spatially varying surface fluxes of heat, water vapor, and emissions. Despite its importance, quantifying SH is challenging in part because its definition can be highly dependent on the end use case. For instance, a metric used in geostatistics for measuring geographic variability in land use may not be particularly useful to an ecologist concerned with how spatially dependent a species population is on surrounding resources. Furthermore, mathematical assumptions central to the choice of metric such as scale similarity may not be applicable across use cases and thus limit the metrics' applicability. This has prompted the development of numerous metrics across disciplines that quantify SH. Here, we discuss various prominent SH metrics that range in applicability and complexity, and point to limitations in these approaches for use in quantifying emissions spatial heterogeneity.

2.1.1 Spatial autocorrelation and semivariograms

Spatial correlation between measurements can be evaluated using correlograms and semivariograms. Correlograms are created by computing the correlation, measured via Pearson's correlation coefficient, between two measurements separated by a given distance. Once the correlation across all distances and associated measurement pairs is computed, correlation is plotted against distance. A similar approach is employed for semivariograms, where the variance is plotted against distance between measurement pairs. Cooper et al. 1997 apply these techniques to determine the spatial correlation in streams between snail density and algal biomass, which serves as an important microhabitat. The authors show how these metrics can be leveraged to quantify the spatial correlation and variability between measurements. While correlograms and semivariograms are useful for explaining the correlation and variance between spatially distributed measurements, they do not provide a one-point statistical measure of how spatially heterogeneous a region is, nor do they provide information on how variance for a quantity of interest is spatially arranged over a region.

2.1.2 Fractal dimensions

A Fractal dimension, or fractional dimension, is a non-integer dimension (Mandelbrot 1967, 1982). Surfaces with greater complexity across spatial scales have higher fractal dimensions and vice versa. Fractal dimensions are scale invariant, meaning that it can be used to evaluate heterogeneity across surfaces of varying area. Loke and Chisholm 2022 discuss their use in ecology and point to numerous important limitations and considerations when utilizing fractal dimensions. The authors note that in practice, measuring fractal dimensions is challenging due to the need to quantify the broad range of scales which may be limited by the resolution of measurement techniques. Additionally real-world objects and surfaces are not truly fractal because self-similarity breaks down at certain scales.

2.1.3 Lacunarity

Surfaces with similar fractal dimensions can have dissimilar variations or texture (i.e., their variance can be arranged in different ways). This led Mandelbrot (1983 or 1982?) to introduce Lacunarity as a metric for quantifying the textural variation of surfaces with similar fractal dimension. Lacunarity is related to the distribution of scales of texture in a surface. Surfaces with a broader range of texture, including large and small gaps and variations, will tend to have high lacunarity. For more homogeneous objects, the distribution

of texture scales will be narrower and will result in a lower lacunarity value. Dong 2000 provide an overview of lacunarity and its use in geography and geographic information science (GIS) applications. They note that lacunarity is often quantified using a gliding box algorithm, for which the researcher must choose the gliding box size. Importantly, changes to the gliding box size do not ensure linear scaling of the difference between lacunarity of multiple patches, meaning that, for instance, a patch may have higher lacunarity compared to other patches at small gliding box sizes but may have lower lacunarity than other patches at larger gliding box size. While this may be a useful attribute of lacunarity if one wishes to evaluate the scale dependence of spatial variability and the scales at which patches appear spatially similar or dissimilar (indeed, this is a primary use case as outlined by Dong 2000), gliding box size introduces an additional parameter one must choose when quantifying spatial heterogeneity and could complicate intercomparison of lacunarity measurements.

2.1.4 Information entropy based metrics

In landscape ecology, information entropy based metrics such as Shannon's evenness index are used to quantify the patchiness of topography that is divided among numerous land uses classes. Plexida et al. 2014 evaluate a number of metrics, including Shannon's evenness index, for measuring the topological variability and land use of central Greece. For its use in landscape ecology, Shannon's evenness quantifies how evenly distributed the various land use types in a region are. It is defined as Shannon's diversity index over N populations (i.e., the Shannon entropy) divided by the maximum diversity index. Shannon's evenness index is useful if evaluating a region with numerous patches that are divided into different categories; however, its use is less apparent for quantifying the spatial heterogeneity of a single scalar field.

2.1.5 Nearest neighbor statistics for point-based heterogeneity

Shu et al. 2019 discuss nearest neighbor distance statistics for use in GIS settings to quantify the spatial heterogeneity of points and apply various metrics to example cases including the spatial distribution of crime events in a city, regional seismic activity in Yutian China, and taxi routes in Beijing China. These examples range from 2D to 4D, illustrating the multidimensional applicability of nearest-neighbor metrics. The authors present a goodness-of-fit metric based on the distribution of nearest neighbor distances called the level of heterogeneity. A normalized version of the metric is proposed to resolve issues that arise when comparing datasets with differing magnitudes due to differences in scale or intensity. The authors note that while

the proposed metric is suitable for capturing point-based spatial heterogeneity, it is quite computationally expensive. It is recommended that alternative nearest-neighbor metrics evaluated alongside the proposed metric should be preferred for computationally intensive datasets.

2.1.6 Multiscale norms

Sobolev norms have been used to quantify the mixing and transport of passive scalars in fluids (Thiffeault 2012). Sobolev norms act as a weighted sum of the Fourier coefficients resulting from the Fourier transform of a scalar field (i.e, the passive scalar suspended in either a fluid or the atmosphere). The multiscale nature of Sobolev norms refers to the selection of Sobolev space H^q over which the norm is defined. Thiffeault 2012 show that the choice of Sobolev norm for $q < 0$ is valuable for flow mixing applications as the magnitude of the norm decays alongside the mixing of the medium.

2.2 Metrics for quantifying the mixing of reactive compounds

Atmospheric constituents that undergo chemical reactions including gas phase and aerosol species are subject to both spatial and temporal constraints that determine the rate at which reactions will proceed. For instance, species must be spatially collocated for reactions to occur, and they must remain in close proximity over the timescale that a given reaction will proceed. This gives rise to two important metrics: (1) segregation intensity, which quantifies the spatial proximity of reactive species and (2) the Damköhler number, which characterizes the dominant timescales governing the reactivity of species.

2.2.1 Segregation intensity

The segregation intensity, first theorized by Danckwerts 1952 for use in combustion processes, is a measure of how spatially segregated or mixed two reactive species are that follow a typical second-order reaction of the form



Using Reynolds decomposition to express each species concentration as the sum of a spatial average and local deviation, $[A] = \overline{[A]} + [A]', [B] = \overline{[B]} + [B]',$ such that the chemical reaction proceeds as

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -k \left(\overline{[A]} \cdot \overline{[B]} + \overline{[A']} \overline{[B']} \right). \quad (2.2)$$

The segregation intensity is then

$$I_s = \frac{\overline{[A']} \overline{[B']}}{\overline{[A]} \cdot \overline{[B]}}, \quad (2.3)$$

such that the chemical reaction can be expressed as

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -k \left(\overline{[A]} \cdot \overline{[B]} \right) (1 + I_s). \quad (2.4)$$

Thus, I_s can be thought of as imposing an effective reaction rate $k^{\text{eff}} = k(1 + I_s).$ When $I_s = -1,$ species A and B are fully spatially separated, such that no reaction occurs. As I_s approaches zero, the two species become fully mixed and the effective reaction rate matches the ideal rate of reaction. I_s can also be positive, corresponding to positive covariance between species which effectively increases the rate of reaction.

2.2.2 Damköhler number

The Damköhler number (Damköhler 1947) relates the turbulence and chemical reaction timescales via the ratio

$$D_a = \frac{\tau_{\text{turb}}}{\tau_{\text{chem}}}. \quad (2.5)$$

The definition of turbulent and chemical timescales varies by application. For the convective boundary layer, Vinuesa and Arellano 2003 adopt the following expression for the Damköhler number,

$$D_a = \frac{z_i}{w_*} k[B], \quad (2.6)$$

where w_* is the velocity scale in the convective boundary layer and is defined as $\left[(g/\Theta_v) \overline{w\theta}_0 z_i \right]^{1/3},$ and where g is gravitational acceleration, Θ_v is virtual potential temperature, $\overline{w\theta}_0$ is vertical heat flux, and z_i is the boundary layer height.

Figure 2.1 displays the three primary regimes for the Damköhler number that determine the abundance of precursor concentrations $[A]$ and $[B].$ When the turbulent and chemical timescales are balanced, $D_a = 1.$ If

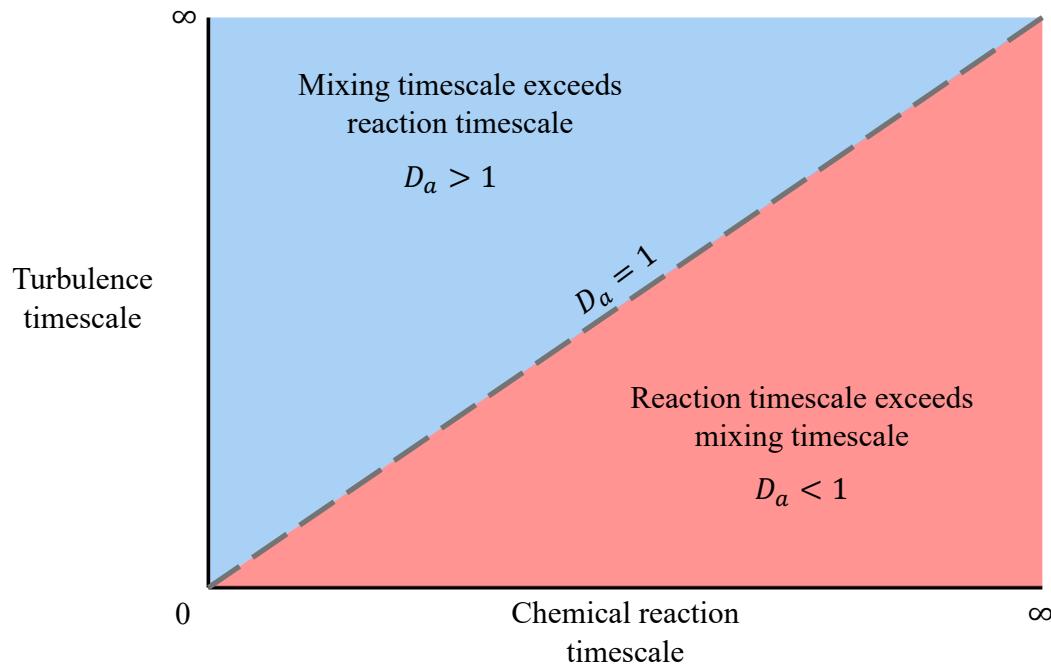


Figure 2.1: Dependence of the Damköhler number on turbulent and reactive timescales. Figure adapted from Kotamarthi and Feng 2017

the chemical reaction timescale is shorter than the turbulence timescale, $D_a > 1$ and the concentration of the precursors will be determined by the rate at which turbulence mixes the reactive compounds (fast-chemistry regime). Conversely, if the chemical reaction timescale is slower than the turbulent timescale, $D_a < 1$ such that the concentration of precursors is determined by the rate of chemical reaction (slow-chemistry regime). Thus, the Damköhler number indicates the relative importance of turbulence in chemical reactions – in the fast chemistry regime with reactions with $D_a > 1$, turbulent scales responsible for mixing the reactive compounds should be fully resolved. Examples of relevant gas-phase reactions in convective boundary layer that correspond to the fast-chemistry regime include oxidation of volatile organic compounds such as isoprene by OH [I assume oxidation of SO₂ by OH as well?].

2.3 A novel approach to quantifying spatial heterogeneity

Existing approaches to quantifying spatial heterogeneity discussed in Section 2.1 and metrics for mixing of reactive compounds in Section 2.2 provide valuable information on the state of a heterogeneously distributed field, however each metric varies in terms of range of applicability, interpretability, and ease of

implementation.

For instance, spatial autocorrelation and semivariograms are relatively easy to interpret and are computationally efficient to measure, but they are primarily useful for capturing the correlation and variability at a single point rather than over an entire region. Alternatively, the nearest neighbor metric proposed by Shu et al. 2019 is useful across a broad range of applications as illustrated by the authors, however, their approach is computationally expensive and is not readily interpretable to the same manner as other spatial heterogeneity metrics. Metrics for mixing provide useful information on how spatially colocated reactive compounds are and the relevant timescales that determine the abundance of precursors, however they do not provide information on how the variance in the spatial distribution of each compound is arranged.

Thus, there exists the need for a novel spatial heterogeneity metric for use in atmospheric science applications including quantifying emissions spatial heterogeneity and subsequent atmospheric field heterogeneity once compounds are emitted into the planetary boundary layer. Mohebalhojeh et al. 2024 (in prep) have developed a new approach to measuring spatial heterogeneity with key benefits being that their approach is broadly applicable, straightforward to interpret, and computationally efficient to measure using a Monte Carlo approach discussed in Section 2.3.2.

2.3.1 Metric definition

The spatial heterogeneity metric, subsequently SH , quantifies the level of heterogeneity for single scalar quantity over a 2-dimensional surface. In this thesis, the scalar of interest is either gas phase or aerosol species and the 2-dimensional surface is either the ground level in the case of emissions or a horizontal plane through the computational domain to quantify atmospheric field heterogeneity within the planetary boundary layer.

SH is calculated by summing up the absolute difference between the mean of a scalar quantity over a rectangular subset of the domain and the domain averaged value for all possible subsets. Over a discrete 2-dimensional grid with N cells along the x-axis and M along the y-axis, there exist

$P = (N(N - 1) + 1)(M(M - 1) + 1)$ total possible rectangular subsets. For a scalar field f defined over some domain S , SH is computed as

$$SH(f, S) = \frac{1}{P} \sum_{\tilde{S} \in \mathbb{R}} |\bar{f}(S) - \bar{f}(\tilde{S})|. \quad (2.7)$$

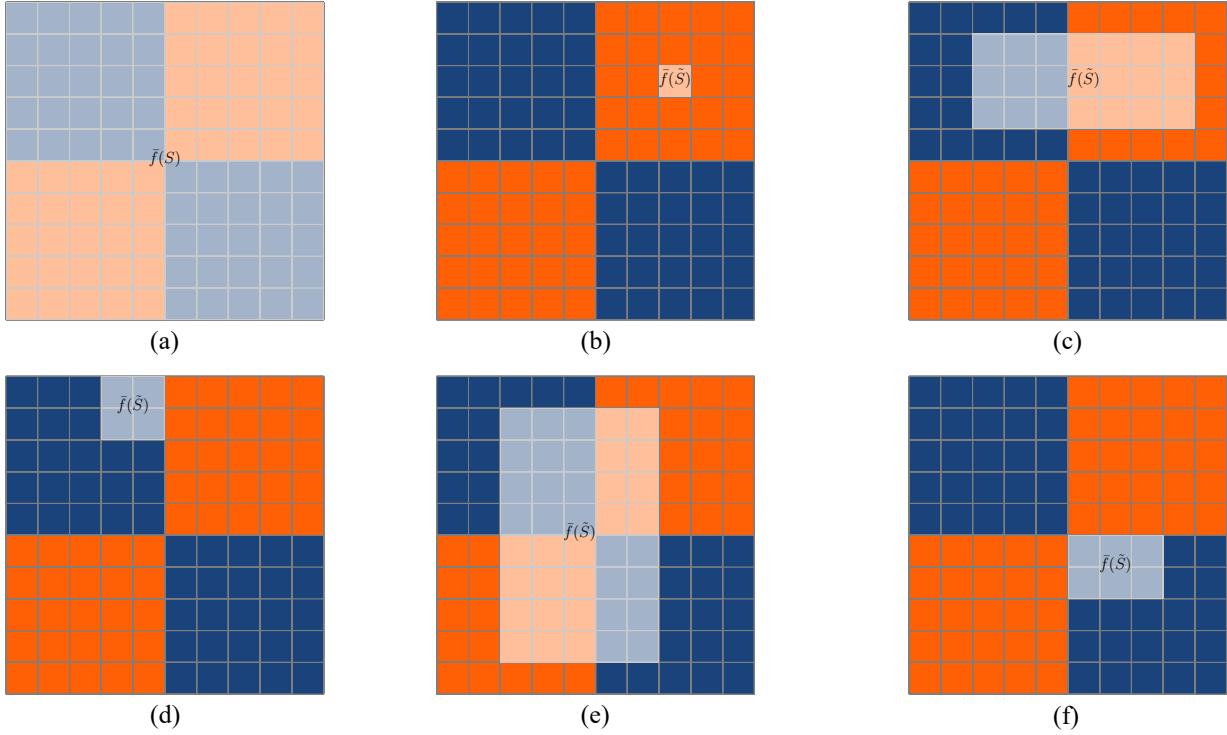


Figure 2.2: Example subsets for SH calculation. (a) Full domain mean. (b-f) Examples of rectangular subsets (highlighted regions) over which the subset mean is computed.

Because the range of gas phase and aerosol emissions varies across orders of magnitude, it is useful to instead utilize a normalized version of the spatial heterogeneity metric,

$$SH(f, S) = \frac{1}{\bar{f}(S) [\frac{3}{2}(N \times M)(N - 1)(M - 1) + N(N - 1) + M(M - 1)]} \sum_{\tilde{S} \in \mathbb{R}} |\bar{f}(S) - \bar{f}(\tilde{S})|. \quad (2.8)$$

A visualization of the total domain mean $\bar{f}(S)$ and domain subset means $\bar{f}(\tilde{S})$ are shown in Figure 2.2. The checkerboard pattern represents an idealized emission pattern, where orange-filled cells correspond to regions of uniform emissions and dark blue regions correspond to zero emissions. $\bar{f}(S)$ is shown in subfigure (a), while five examples of rectangular subsets are displayed in subfigures (b-f).

2.3.2 Computational methods for computing the spatial heterogeneity metric

To calculate SH over a computational domain, an array comprising the scalar quantity of interest with dimension equal to the size of the domain (N by M) is passed to a Fortran subroutine. Here, we discuss two approaches to calculating SH : a computationally expensive naive looping algorithm and a significantly more efficient Monte Carlo based method.

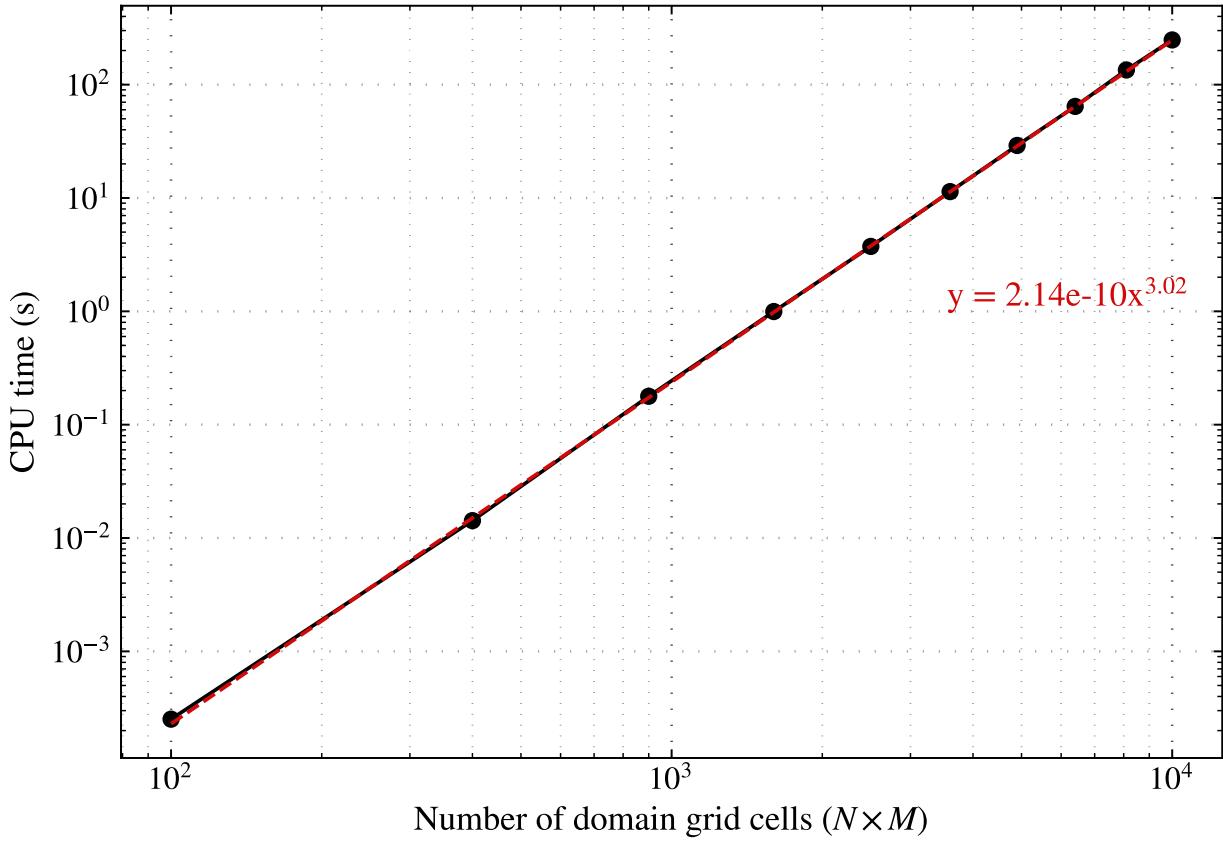


Figure 2.3: CPU time for the naive looping SH Fortran subroutine. The x-axis indicates the total number of domain grid cells (elements) in the array passed to the subroutine. A power law regression is plotted as the red dashed line.

The naive subroutine loops over all possible rectangular subdomains which can be quite computationally expensive, especially for domains with a large number of grid cells (e.g., 100×100 grid cells laterally as used for domain mesh size in this thesis). Figure 2.3 shows the computational scaling for a Fortran subroutine using this naive looping algorithm. A power law regression (red dashed line) is fit to the CPU time vs. the total number of domain grid cells. The naive looping algorithm scales as $O(n^3)$ for n the number of grid cells. For domain sizes used in this thesis ($N = M = 100$), this results in a single calculation taking in excess of 2 minutes.

Instead of looping over every possible subdomain, we may use the fact that the probability of selecting any given subdomain is the same (i.e., the sampling probability is uniform across the entire domain) in order to construct a Monte Carlo sampling based approach for calculating SH . We then pass the array with domain scalar values alongside a parameter for the number of subsets to sample ($N_{\tilde{S}}$) to our Monte

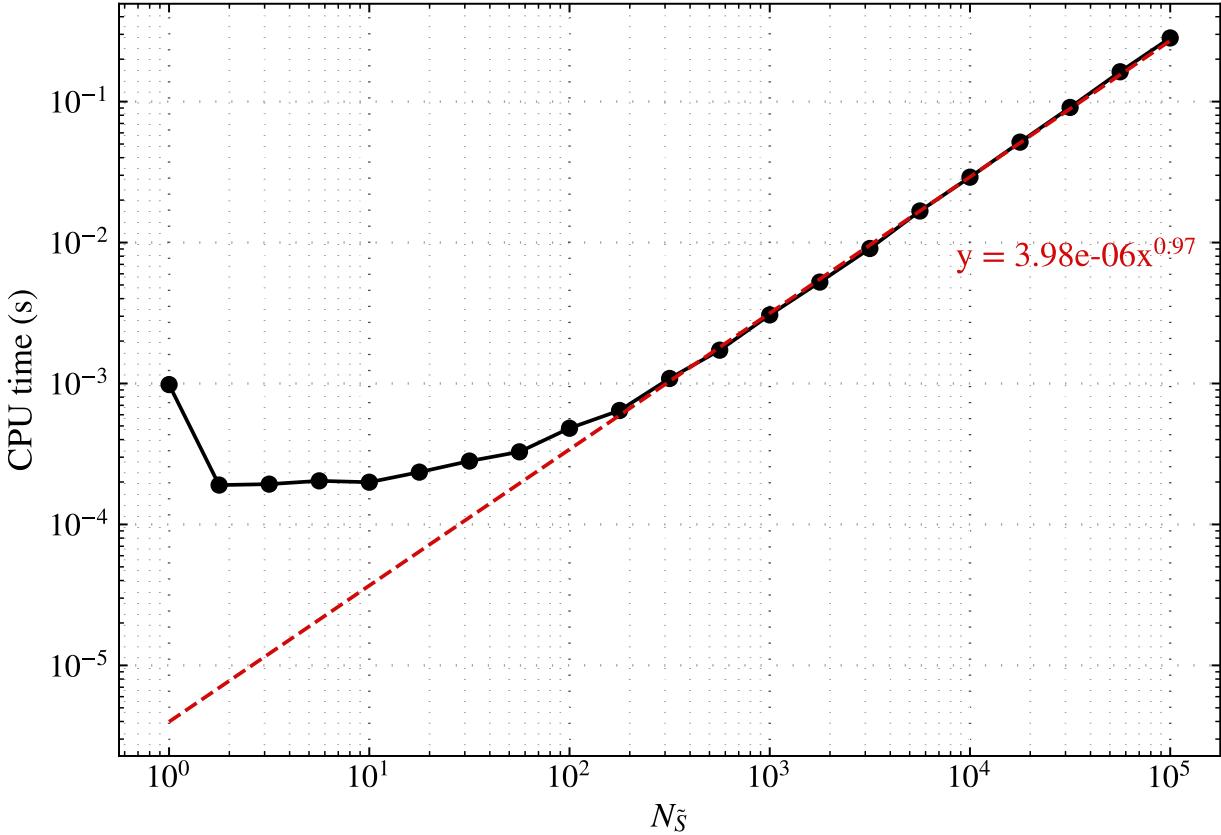


Figure 2.4: CPU time for the Monte Carlo SH Fortran subroutine. The x-axis indicates the number of domain subsets that are randomly selected to determine the SH estimate. A power law regression is plotted as the red dashed line.

Carlo-based Fortran subroutine. Figure 2.4 shows the CPU time for corresponding number of randomly selected domain subsets, ranging from 1 to 100,000 for a domain with dimensions $N = M = 100$ and $P = (100(100 - 1) + 1)(100(100 - 1) + 1) = 98,029,801$ total subsets. For a low number of randomly selected subsets (number of subdomains $\lesssim 100$), the algorithm scales quite weakly, suggesting that computational overhead limits speedup in this region over the naive algorithm. As the number of subdomains increases above 100, the algorithm scales as $O(N_{\tilde{S}})$ as indicated by the power law regression.

We validate the accuracy of the Monte Carlo sampling subroutine against the naive looping approach in Figure 2.5. First, the precise value of SH was computed via the naive algorithm for a scalar field of random noise with dimensions $N = M = 100$. We then vary the number of randomly selected subsets $N_{\tilde{S}}$ used to compute the estimate of SH in the Monte-Carlo subroutine. The left panel in Figure 2.5 shows how the SH estimate converges on the precise value of SH (shown as a horizontal black dashed line). The right

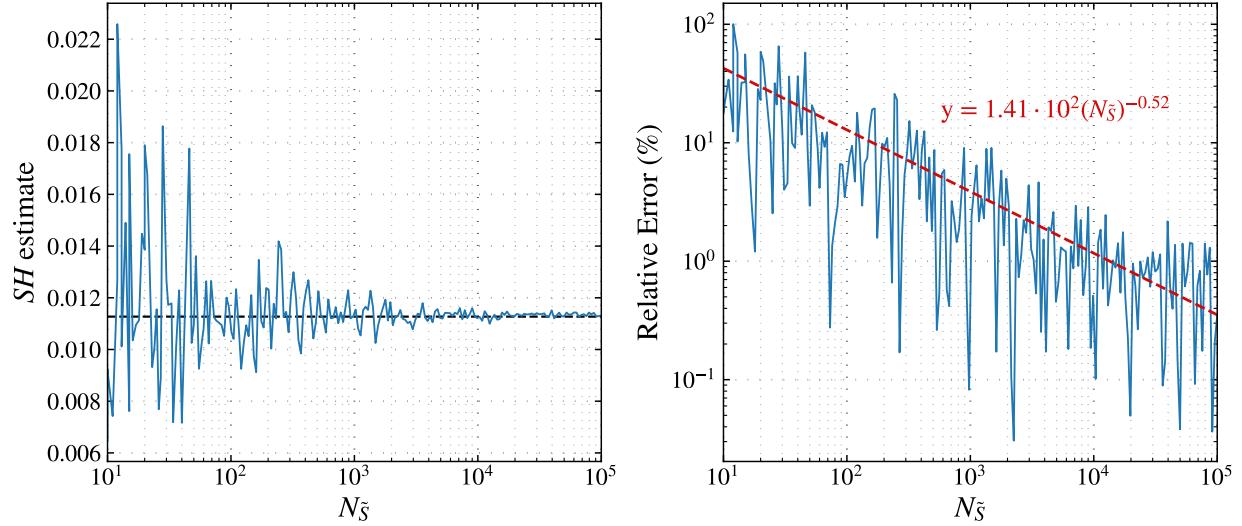


Figure 2.5: SH estimate in blue for the Monte Carlo sampling subroutine vs. the number of randomly selected domain subsets (top panel). The true value of SH computed via the naive algorithm is shown as the black line. Absolute relative error between SH estimate and the true value of SH (middle panel). Bias between SH estimate and the true value of SH (bottom panel)

panel displays the relative error between SH estimates and the precise value (note the logarithmic scaling). Relative error decreases as $\propto 1/\sqrt{N_{\bar{S}}}$ as indicated by the power law regression in red. This behavior is to be expected, because as the number of samples (i.e., $N_{\bar{S}}$) increases, the error should decrease like the standard error— $SE = \sigma/\sqrt{n}$ for σ the standard deviation of a sampling distribution and n the number of samples.

Given the performance of the Monte Carlo sampling subroutine over the naive looping approach and its ability to reach a high level of accuracy with minimal error when sampling a sufficient number of domain subsets, we utilize the Monte Carlo method for subsequent SH calculations. For such calculations, we choose the number of randomly selected domain subsets to be 10,000 as this results in relative error $\sim 1\%$ for the domain size $N = M = 100$ used in this thesis. Referring back to Figures 2.3 and 2.4 for naive algorithm performance and Monte Carlo sampling performance, respectively, we find that for a domain size with $N = M = 100$, CPU time is in excess of two minutes for the naive looping approach and of order ~ 0.1 s for the Monte Carlo subroutine. This corresponds to a speedup in excess of 1000.

2.3.3 Example calculations for emission patterns

We calculate the spatial heterogeneity for 6 emission scenarios shown in Figure 2.6. Emission patterns are ordered from low to high SH , ranging from uniform emissions across the domain (“Uniform Base Case”) to

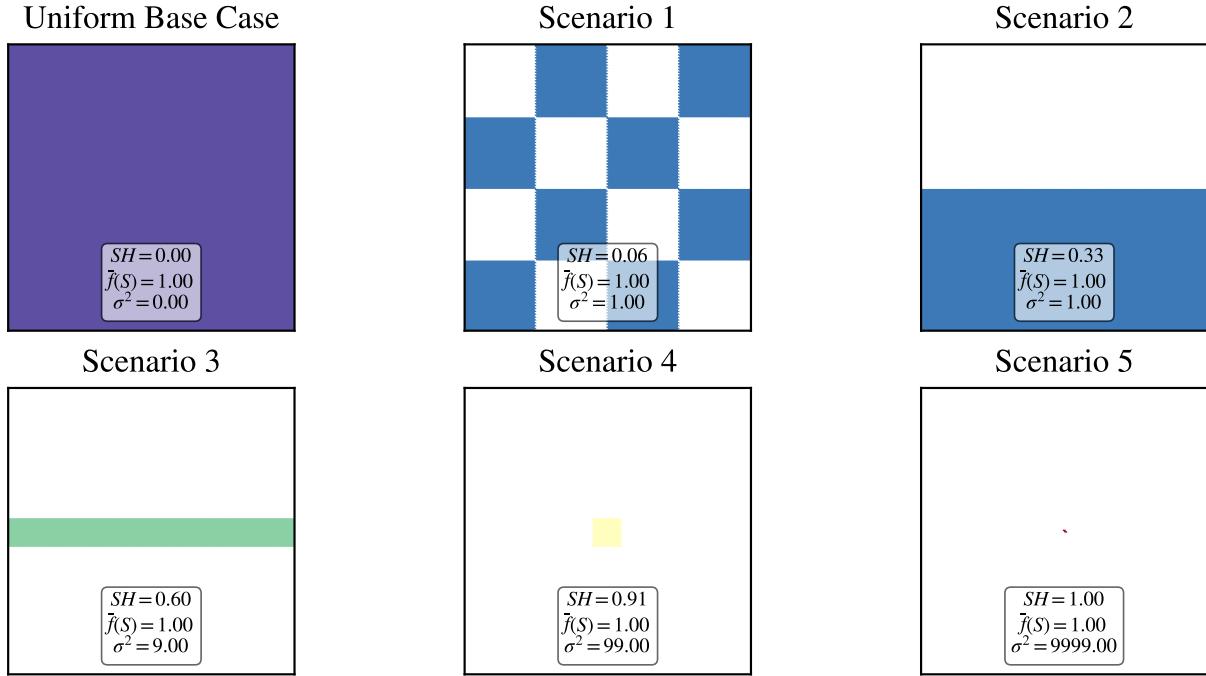


Figure 2.6: Example emission patterns arranged from least heterogeneous (“Uniform Base Case”) to most heterogeneous (“Scenario 5”). For each pattern, the spatial heterogeneity SH is listed alongside the domain mean ($\bar{f}(S)$) and variance (σ^2). The color of each scenario indicates the emission scaling relative to the uniform base case with red being the highest scaling.)

highly heterogeneous localized emissions. Note that the total mass of emissions per unit time is the same across all scenarios. The emissions scaling rate is adjusted based on the area each pattern occupies relative to the base case and is indicated by the color of each emission region (dark blue corresponds to scaling closer to unity while red indicates the greatest magnitude of scaling).

For each scenario, the domain mean, $\bar{f}(S)$, and variance, σ^2 , are shown in addition to SH . Note that the variance of the checkerboard scenarios 1 and 2 are all equal to 1.0 while the SH increases across these scenarios. This highlights an important attribute of the spatial heterogeneity metric—the SH metric provides information not only on how variable an emission pattern is across the domain, but also is sensitive to how the variance is arranged. This marks an advantage of the SH metric over previously discussed metrics, including semivariograms, fractal dimensions, and information entropy statistical measures that are insensitive to changes in the distribution of variance over the scalar field of interest.

Chapter 3

Modeling tools

This chapter discusses the modeling tools necessary for conducting simulations presented in this thesis. A description of the transport treatment, large-eddy simulations, is provided alongside discussion of requisite sub-grid scale parameterizations that we utilize. Attributes of the computational domain, including its spatial extent, grid resolution, and other defining qualities are presented. Meteorological initial conditions for simulations are discussed as well as determination of necessary spin-up time for the development of convective boundary layer in the computational domain. Subsequently, chemical mechanisms used for gas phase and aerosol chemistry are discussed. Lastly, the aerosol model, PartMC, and its coupling with the chosen transport model is discussed.

3.1 Large-eddy simulations

Within the planetary boundary layer (PBL), turbulent eddies are responsible for mixing and transporting gases and aerosol particles as well as thermal and kinetic energy. Over time, these eddies break down due to flow instabilities, frictional losses due to interactions with physical boundaries, and the viscosity of the atmospheric constituents. Therefore, it is important for modeling frameworks that represent the PBL to explicitly resolve the physical scales over which transport and mixing occur, as well as accurately model the dynamical tendency of kinetic energy transfer from large to small eddies.

Representation of turbulence in modeling frameworks is a computationally challenging task because of the range of scales one must consider and the associated need for high spatial resolution. In the PBL, turbulent eddies range in size from hundreds of meters to the Kolmogorov length scale on the order of a few millimeters (Kolmogorov 1991), at which size eddies break down due to kinematic viscosity of atmospheric constituents. A widespread technique when modeling the PBL is the use of large-eddy simulations (LES). In LES, the equations of motion are filtered such that the largest, energy-containing eddies are explicitly

resolved down to a grid resolution on the order of 10 meters. For eddies smaller than the resolution of the grid, sub-grid scale (SGS) parameterizations are used to represent the statistical attributes of unresolved eddies, including their energy dissipation and stress forces.

For simulation results presented in this thesis, we use the Weather Research and Forecasting model (WRF) configured for LES (Skamarock et al. 2008). In practice, conducting LES studies in WRF arises from modeling choices including the representation of SGS turbulence parameterizations and adequately high grid resolution; that is, there is no “switch” for configuring WRF in LES mode, but rather structural choices which permit representation of the relevant dynamics.

3.1.1 Sub-grid scale parameterizations

A key choice in the implementation of LES is the selection of SGS turbulence parameterizations. Specifically, one must parameterize the SGS stress τ_{ij} and SGS flux q_i . The stress tensor τ_{ij} represents the deformational forces acting both normal ($i = j$) and perpendicular ($i \neq j$) to each grid cell, while the SGS flux q_i refers to the transport of scalars such as momentum, heat, or other quantities by unresolved eddies. A common technique for the closure of SGS stress and flux is the use of eddy-viscosity models. This technique was pioneered by Smagorinsky for parameterizing the motion of SGS eddies in a model of general circulation (Smagorinsky 1963). Eddy-viscosity models mimic the linear relationship between the stress tensor of a Newtonian fluid and shearing forces acting on the fluid scaled by the fluid’s molecular viscosity. As such, eddy-viscosity models are not fundamentally grounded in physical tendencies of turbulent flows, but rather provide an empirical approximation that mimics Newtonian fluids and has been shown to be reasonable for representing SGS turbulence in modeling studies of the PBL (Stoll et al. 2020). The SGS stress and SGS flux are then expressed as

$$\tau_{ij} = -2v_T \tilde{S}_{ij}, \quad (3.1)$$

$$q_i = -v_\theta \frac{\partial \tilde{\theta}}{\partial x_i}, \quad (3.2)$$

where v_T is the eddy viscosity coefficient, $\tilde{S}_{ij} = \frac{1}{2}(\partial \tilde{u}_i / \partial x_j + \partial \tilde{u}_j / \partial x_i)$ is the resolved strain rate tensor (i.e., the rate at which straining forces such as expansion and shearing due to resolved flow occur), v_θ is the eddy diffusivity coefficient for some scalar quantity θ , and $\partial \tilde{\theta} / \partial x_i$ is the resolved-scale gradient of scalar θ in direction x_i . As \tilde{S}_{ij} and $\partial \tilde{\theta} / \partial x_i$ are known quantities determined at the resolved scale, eddy-diffusivity

models then become a matter of determining v_T and v_θ .

Deardorff was the first to implement Smagorinsky's eddy-diffusivity SGS model for LES, however, he found that the model was overly diffusive for short wavelength features (Deardorff 1970). Deardorff 1980 instead proposed an alternative eddy-diffusivity model in which a prognostic equation for SGS kinetic energy E is solved alongside expressions for v_T and v_θ

$$\frac{\partial E}{\partial t} = -\frac{\partial \tilde{u}_j E}{\partial x_j} + 2v_T \tilde{S}_{ij} \tilde{S}_{ij} - v_\theta \frac{\partial \tilde{b}}{\partial z} + \frac{\partial}{\partial x_j} 2v_T \frac{\partial E}{\partial x_j} - \epsilon, \quad (3.3)$$

$$v_T = C_1 \ell \sqrt{E}, \quad (3.4)$$

$$v_\theta = \left(1 + 2 \frac{\ell}{\Delta}\right) v_T, \quad (3.5)$$

where b is buoyancy, ϵ is the turbulent kinetic energy (TKE) dissipation, C_1 is a coefficient that must be specified by the modeler, and ℓ is the turbulent length scale. In this thesis, we use Deardorff's TKE scheme for eddy diffusivity. Customarily, $C_1 = 0.1$ and we use this value as recommended by an idealized test case for LES simulations packaged alongside the WRF codebase.

3.1.2 Computational domain

We model the PBL in an 3D idealized domain with dimensions 10 km in both lateral dimensions and 2 km vertically. A horizontal resolution of 100 m was chosen alongside a vertical resolution of approximately 20 m¹, resulting in a domain of 100x100x100 grid cells. This resolution is necessary to resolve eddies responsible for turbulent transport in the PBL. A higher resolution vertically is desired in order to accurately represent vertical motions due to convective and turbulent transport. Time discretization is set to 1 second for all simulations, however sub-models such as chemistry (when active) further refine time discretization to maintain stability for integration.

The domain is absent of any topographic features with a uniform, flat surface. Latitude and Longitude coordinates of (0, 0) are used internally for computing the solar zenith angle necessary for photolysis calculations, however, the domain's idealized topography is not intended to match the geographic region surrounding these coordinates.

¹WRF uses a terrain-following pressure “eta” coordinate system for vertical levels. Note that because the domain only extends to 2 km vertically, vertical levels are nearly equally spaced apart.

3.1.3 Meteorological Initial Conditions

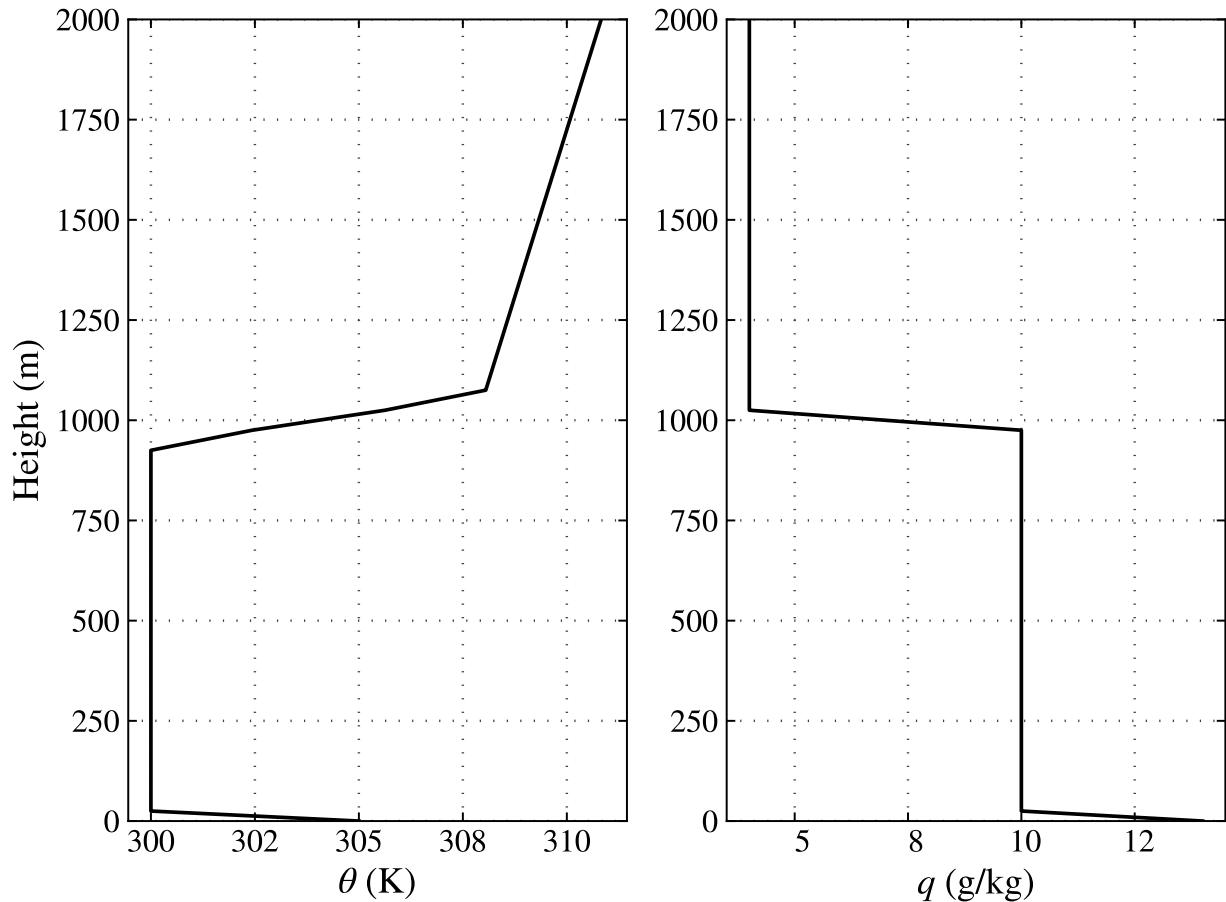


Figure 3.1: Idealized atmospheric sounding used for domain meteorological initial conditions. Initial conditions for potential temperature (left) and specific humidity (right). TODO: check what is best, units in brackets or in parentheses? Figure 3.2 uses brackets so I should be consistent either way...

The domain meteorological conditions are initialized using an ideal sounding typical of a convective boundary layer (see Figure 3.1). The lowest 25 m of the atmosphere are initially unstable to allow for parcels to rise due to buoyancy into the neutral PBL that extends to approximately 1 km. Above this point, the PBL is capped by an inversion up to 2 km.

Both zonal (u) and meridional (v) wind are set to zero throughout the entire domain. Tian et al. 2022 and Fast et al. 2019 both show that the impact of surface heterogeneities in surface heat fluxes on cloud formation and type are sensitive to wind conditions, and are most pronounced for minimal background winds. Extending the relevance of these findings to this thesis, our choice of an initial condition characterized by zero winds is intended to isolate the impact of emissions spatial heterogeneity on the evolving atmospheric

state of gasses and aerosols.

At the surface, the specific humidity q is highest at 14 g kg^{-1} and lowers to a uniform 10 g/kg within the PBL. Above the PBL, q is a uniform 4 g kg^{-1} extending vertically to the top of the domain. At the surface, a uniform surface heat flux of 0.24 K ms^{-1} is set and random perturbations of the temperature field are imposed at the lowest four levels to initiate turbulence. The surface heat flux is responsible for maintaining convection and turbulent transport over the course of the simulation. Boundary conditions are periodic along all lateral boundaries.

3.1.4 Simulation spin-up

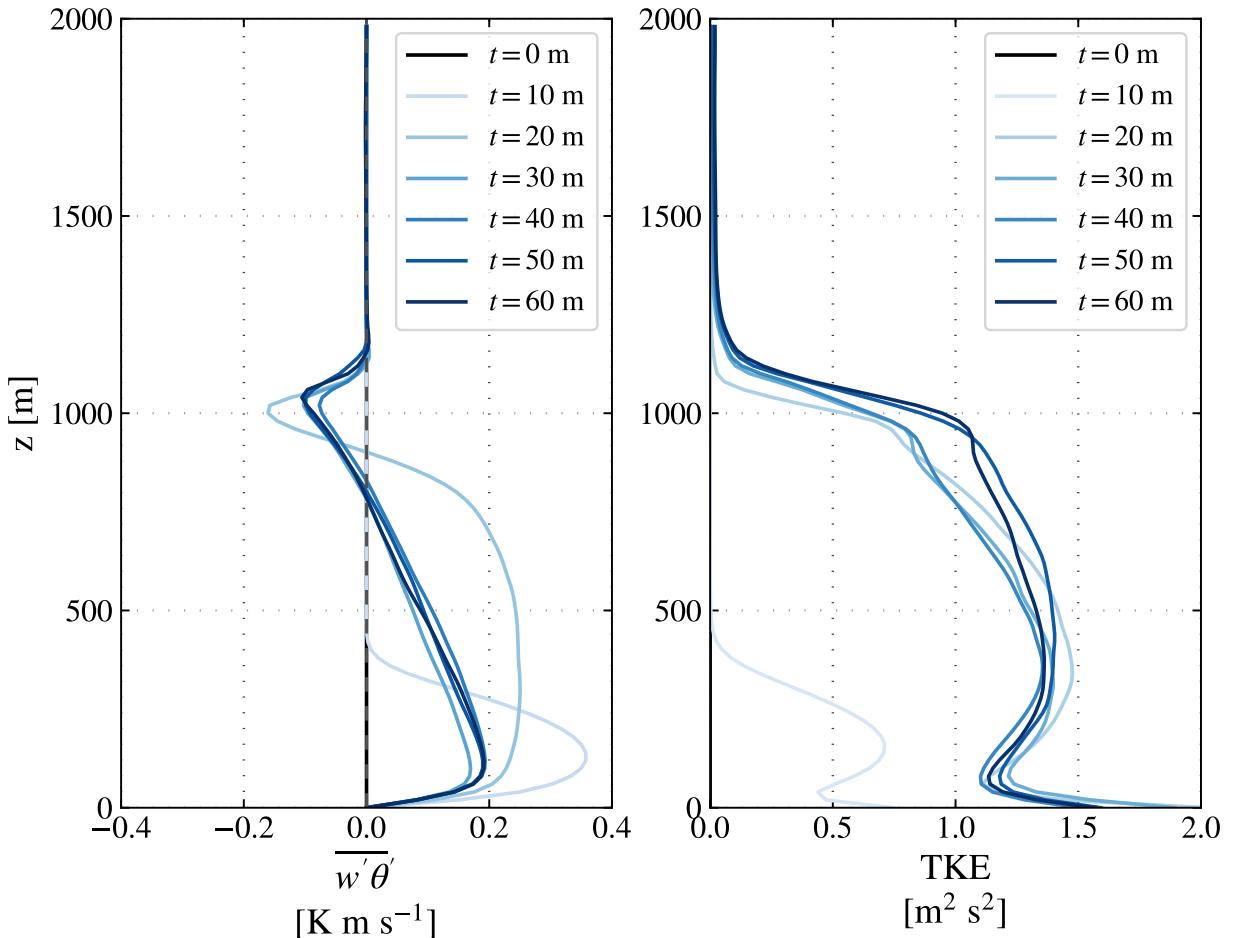


Figure 3.2: Resolved-scale vertical heat flux profiles (left) and TKE at intervals of 10 minutes during the first hour of simulation spin-up.

Prior to the release of gas and aerosol emissions, the simulation is allowed to spin up for a period of 1 hour.

During this time, convection and turbulence within the boundary become well established and thoroughly mix the initial conditions for gases and aerosols alongside transporting heat and momentum. In a well established convective boundary layer, the profile of vertical heat flux should decrease approximately linearly with height. Both resolved-scale² vertical heat flux and TKE profiles are shown in Figure 3.2 in increments of 10 minutes from $t = 0$ minutes to $t = 1$ hour. Initially, vertical heat flux is zero everywhere due to the initial condition of zero vertical velocity. At $t = 10$ minutes, vertical heat flux is localized near the surface and exceeds 0.3 K m s^{-1} . By $t = 30$ minutes, initial transient behavior in vertical heat flux relaxes as the convective boundary layer becomes more well established and the heat flux profile takes on a linearly decreasing trend with height. Profiles for subsequent times agree closely with the profile at $t = 30$ minutes, indicating that the convective boundary layer is near fully established by 30 minutes. Note that the TKE profiles in Figure 3.2 indicate that energy-containing eddies in the upper boundary layer continue to develop through $t = 1$ hour, as TKE increases in the upper boundary layer from $\sim 0.7 \text{ m}^2 \text{s}^{-2}$ at $t = 30$ minutes to $\sim 1.1 \text{ m}^2 \text{s}^{-2}$ by $t = 1$ hour. Thus 1 hour of model spin-up time was chosen to adequately allow for development of the convective boundary layer and resolved scales of turbulence.

3.2 Gas phase simulations

3.2.1 Chemical mechanism

In Chapter 4, we evaluate the impact of emissions spatial heterogeneity on gas phase reactions with a particular focus on ozone production. We select the chemical mechanism Carbon-Bond Mechanism-Z (CBMZ) for gas phase photochemical reactions (Zaveri and Peters 1999). CBMZ models both inorganic and organic compounds prevalent in anthropogenic and biogenic emissions. CBMZ allows computationally efficient calculation of over 100 reactions across dozens of chemical species. This is possible due to the model’s “lumped-structure” approach to sorting similar organic compounds by their carbon bond structure (e.g., alkanes, carbonyls, etc.). This reduces the need for tracking large volumes of organic species and reactions. Despite simplifications to the organic chemistry mechanism, CBMZ has been shown to accurately represent concentrations of compounds of primary interest for atmospheric chemistry applications (e.g., O_3 , NO_x , etc.) (Zaveri and Peters 1999).

²Ideally, one would evaluate total (resolved + parameterized) vertical heat flux and total TKE. WRF does not provide output for SGS quantities, so it would be necessary for one to modify the codebase to allow exporting these additional data.

3.2.2 Initial conditions and emissions

Table 3.1: Gas phase emissions and initial conditions. Table adapted from N. Riemer et al. 2009 with permission.

Species	Symbol	Initial Mole Fraction (ppb)	Emissions ($\text{nmol m}^{-2} \text{ s}^{-1}$)
Nitric oxide	NO	0.1	31.8
Nitrogen dioxide	NO ₂	1.0	1.67
Nitric acid	HNO ₃	1.0	
Ozone	O ₃	50.0	
Hydrogen peroxide	H ₂ O ₂	1.1	
Carbon monoxide	CO	21	291.3
Sulfur dioxide	SO ₂	0.8	2.51
Ammonia	NH ₃	0.5	6.11
Hydrogen chloride	HCl	0.7	
Methane	CH ₄	2200	
Ethane	C ₂ H ₆	1.0	
Formaldehyde	HCHO	1.2	1.68
Methanol	CH ₃ OH	0.12	0.28
Methyl hydrogen peroxide	CH ₃ OOH	0.5	
Acetaldehyde	ALD2	1.0	0.68
Paraffin carbon	PAR	2.0	96
Acetone	AONE	1.0	1.23
Ethene	ETH	0.2	7.2
Terminal olefin carbons	OLET	$2.3 \cdot 10^{-2}$	2.42
Internal olefin carbons	OLEI	$3.1 \cdot 10^{-4}$	2.42
Toluene	TOL	0.1	4.04
Xylene	XYL	0.1	2.41
Lumped organic nitrate	ONIT	0.1	
Peroxyacetyl nitrate	PAN	0.8	
Higher organic acid	RCOOH	0.2	
Higher organic peroxide	ROOH	$2.5 \cdot 10^{-2}$	
Isoprene	ISOP	0.5	0.23
Alcohols	ANOL		3.45

Gas phase initial conditions and emissions are chosen to represent species and concentrations typical of an urban plume and are adopted from N. Riemer et al. 2009. The authors determined gas phase concentrations and emission rates via the 1987 Southern California Air Quality Study (SCAQS) data set which contains measurements of both gas phase species and particulate matter mass concentrations collected at multiple sites across the Los Angeles basin (Zaveri, Easter, et al. 2008). Table 3.1 contains all gas phase initial conditions and emission rates Note if I didnt end up using some of these species then remove those. Empty entries

signify zero concentrations or emission rates. To allow for simulation spin-up, all emission rates are set zero during the first hour of simulations. Subsequently, emitted compounds are released only at the surface and at a constant rate as specified in Table 3.1 for the remainder of the simulation.

3.3 Multiphase simulations

3.3.1 Chemical mechanism

Chapter 5 presents simulation results where both gas phase chemistry and aerosol processes (e.g., coagulation, gas-particle partitioning, etc.) are modeled. Both gas phase and aerosol chemistry is represented using the Model for Simulating Aerosol Interactions and Chemistry (MOSAIC) (Zaveri, Easter, et al. 2008). MOSAIC was developed by the authors of CBMZ, and it should be noted that CBMZ is included a sub-model within MOSAIC for handling gas phase chemistry. For aerosol chemistry, MOSAIC simulates dynamic gas-particle partitioning and phase-dependent thermodynamic equilibrium. A key challenge for modeling aerosol chemistry is that the coupled system of solid-liquid phase reactions that govern aerosol thermodynamic equilibrium is often numerically stiff due to the rate of reactions varying over large timescales. Often, chemical mechanisms solve such stiff systems in a computationally expensive manner either by iterative techniques or by directly minimizing the Gibbs Free energy of the system. MOSAIC takes an alternative approach whereby the system of equilibrium reactions is reformulated as a pseudo-transient system. This recasts the system as ordinary differential equations, for which standard numerical techniques are used to integrate and obtain equilibrium steady state solutions. This approach makes MOSAIC computationally efficient while maintaining good agreement when benchmarked against numerically rigorous and accurate models (Zaveri, Easter, et al. 2008).

3.3.2 Aerosol representation

We use the Particle Monte Carlo (PartMC) model for particle-resolved representation of aerosols (N. Riemer et al. 2009). In PartMC, aerosol particles are represented via a set of computational particles with appropriate multiplicity to represent the desired aerosol population. Each computational particle is allowed to compositionally vary due to aerosol processes (e.g., coagulation, condensation, gas-particle partitioning, etc.), thus allowing the representation of a far greater degree of compositional diversity and aerosol properties than sectional or modal based aerosol models (citations - maybe the mixing state review article that had

a good description of aerosol treatments?). PartMC is a box model, meaning that within computational grid cells, the position of computational particles is not tracked. Instead, processes such as coagulation are handled in the probabilistic manner of Gillespie 1975. PartMC is coupled with MOSAIC, thereby leveraging the computational efficiency and accuracy of each model in allowing full representation of an aerosol state (number and mass concentration, per-particle composition) under aging due to both aerosol physical processes and chemical reactions.

Curtis, Nicole Riemer, and West 2017 coupled PartMC-MOSAIC with WRF for a single column model of the planetary boundary layer. The authors developed approaches for modeling the turbulent diffusion and dry deposition of aerosol particles as stochastic processes. The resulting modeling framework, WRF-PartMC-MOSAIC, is extended here for use with 3D LES.

For WRF-PartMC-MOSAIC-LES, we use 100 computational particles per grid cell for a total of 100 million computational particles throughout the domain at initialization. This value was chosen to balance computational efficiency and storage demands alongside numerical representability – too few computational particles will result in random noise for aerosol population properties due to the stochastic nature of the PartMC model.

3.3.3 Initial conditions and emissions

Initial conditions and emissions of gas phase species match those discussed in Section 3.2.2 and are displayed in Table 3.1. Similarly, aerosol initial conditions and emission rates are adopted from N. Riemer et al. 2009, who based aerosol distributions, composition, and emission rates off measurements collected as part of the SCAQS campaign in the Los Angeles valley. Aerosol initial conditions and emission properties are summarized in Table 3.2. Size distributions for aerosol initial conditions and emissions are shown in Figure 3.3 and Figure 3.4, respectively. The aerosol initial condition is comprised of two modes, including a Aitken mode and accumulation mode. Each mode is an equal mixture of 50% ammonium sulfate and 50% primary organic aerosol (POA). Three emission modes are chosen to represent emissions from various urban combustion sources, including cooking, diesel vehicles, and gasoline vehicles. The cooking emission mode is comprised of 100% POA and the diesel and gasoline modes are each a mixture of POA and black carbon (BC).

Table 3.2: Aerosol emissions and initial conditions. Table adapted from N. Riemer et al. 2009 with permission.

Initial/Background	N (m^{-3})	D_{gn} (μm)	σ_g	Composition by Mass
Aitken Mode	$3.2 \cdot 10^9$	0.02	1.45	50% $(\text{NH}_4)_2\text{SO}_4$, 50% POA
Accumulation Mode	$2.9 \cdot 10^9$	0.116	1.65	50% $(\text{NH}_4)_2\text{SO}_4$, 50% POA
Emissions	E ($\text{m}^{-2} \text{s}^{-1}$)	D_{gn} (μm)	σ_g	Composition by Mass
Meat cooking	$9 \cdot 10^6$	0.086	1.9	100% POA
Diesel vehicles	$1.6 \cdot 10^8$	0.05	1.7	30% POA, 70% BC
Gasoline vehicles	$5 \cdot 10^7$	0.05	1.7	80% POA, 20% BC

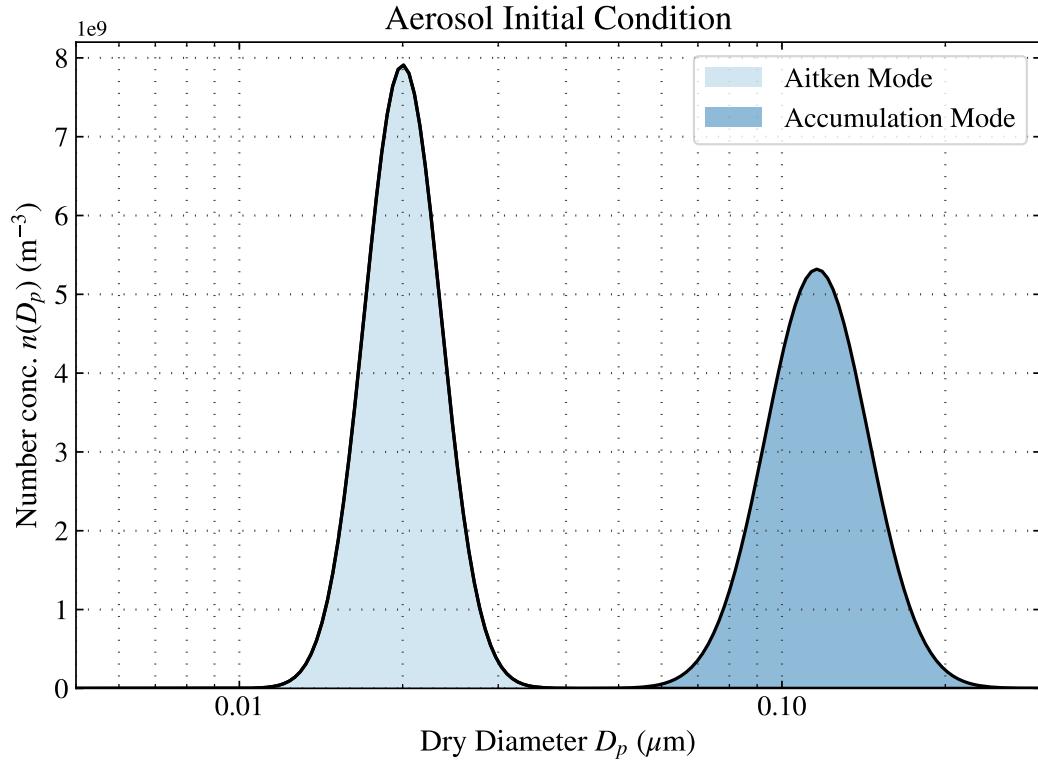


Figure 3.3: Aerosol initial condition size distributions.

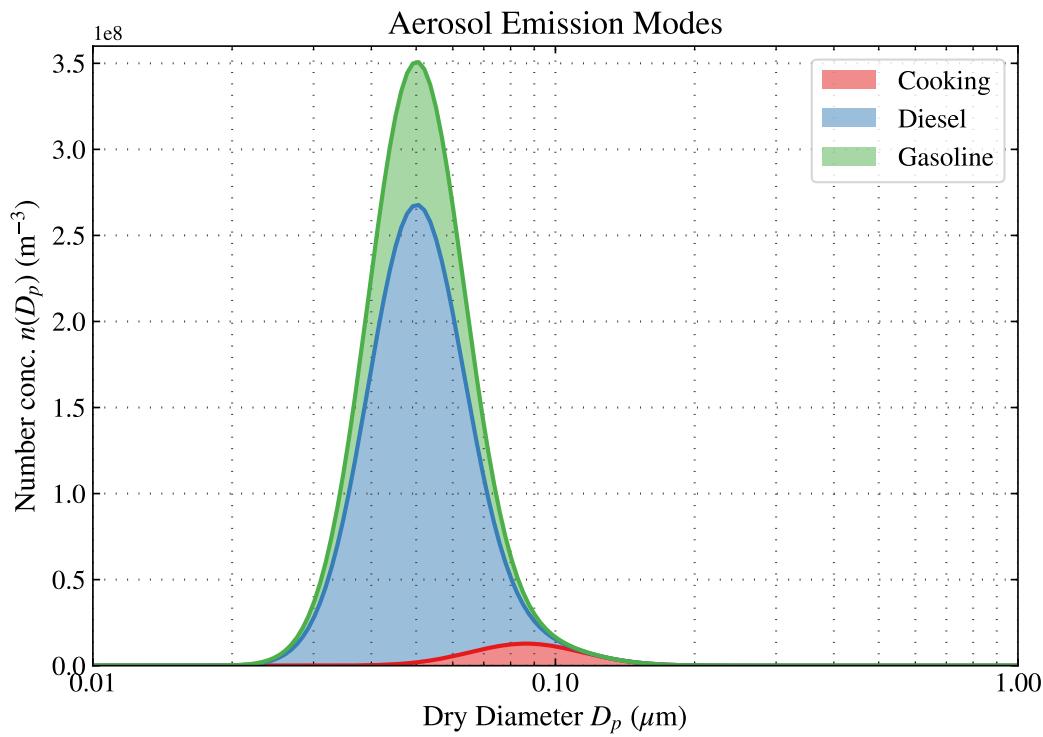


Figure 3.4: Aerosol emission size distributions.

Chapter 4

Impacts of emissions spatial heterogeneity on gas-phase reactions

This chapter investigates the impacts of gas phase emissions and associated chemical reactions on the production of ozone in the planetary boundary layer. The effect emissions spatial heterogeneity on ozone production is explored across numerous emissions scenarios with ranging emissions spatial heterogeneity. We find that for the most heterogeneous emissions case, ozone production is reduced in the mid-boundary layer by up to $\sim 13\%$. We also evaluate the spatial heterogeneity of ozone and its precursor compounds NO_x and volatile organic compounds (VOCs) after they are emitted. We find that SH varies considerably across precursors and also exhibits spatio-temporal variability.

4.1 Simulated emission scenarios

We conduct four simulations in total ranging in emissions spatial heterogeneity from $SH = 0$ to $SH = 1$ for precursor species responsible the production of ozone. Emissions scenarios are shown in Figure 4.1. The first simulation, named the uniform base case scenario, is characterized by uniform emissions of all compounds across the computational domain ground level. The uniform base case has a spatial heterogeneity equal to zero. This scenario represents the emissions across a single grid cell in a lower resolution model, such as a regional or global climate model, where emitted species are both uniform and dilute. Thus, results for simulations with higher emissions heterogeneity are compared against the uniform base case to quantify the structural uncertainty in ozone concentrations resulting from the assumption of uniform, dilute emissions characteristic of coarser resolved models that do not adequately resolve the true emissions spatial heterogeneity.

Across the simulated emission scenarios, the area occupied by ground level emissions decreases up to a single grid cell in the case of emissions scenario 3. This scenario is meant to represent a highly localized emissions source and is the maximally heterogeneous case with $SH = 1$. The total mass per unit time emitted

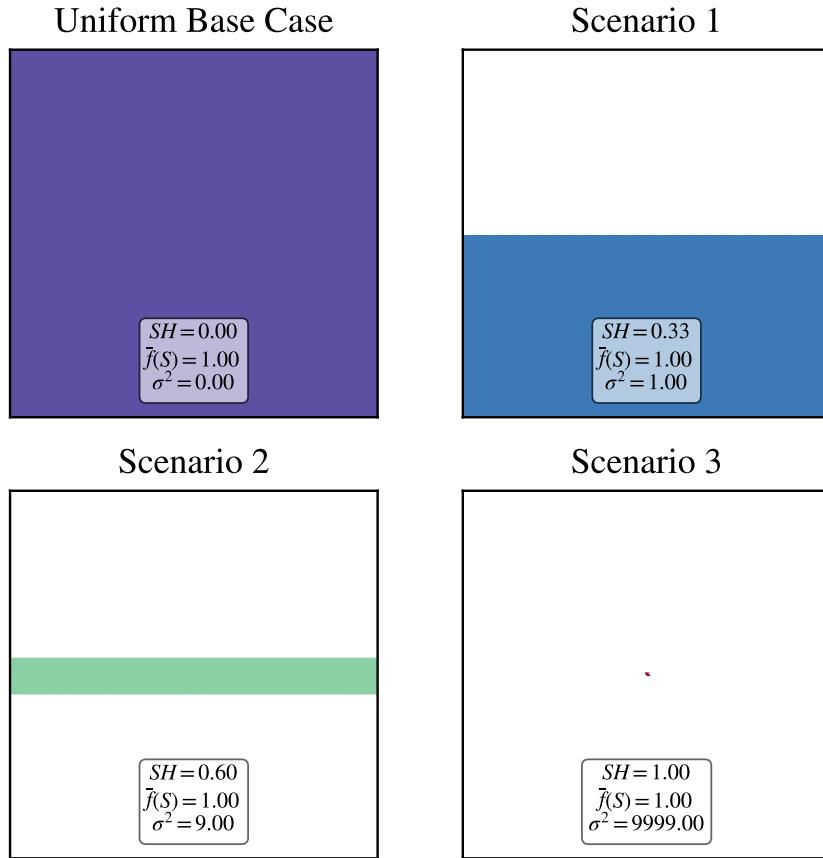


Figure 4.1: Emissions scenarios for ozone production simulations. The spatial heterogeneity of each emission scenario is listed in the lower portion of each scenario alongside domain mean and variance.

across each scenario remains the same, thus the emission rate for high spatial heterogeneity cases must be scaled by the ratio between the area occupied by emissions in the uniform base case and the area emissions occupy in the corresponding emissions scenario. For example, the area of emissions in emissions scenario 3 is 0.01 km^2 while the area occupied by emissions in the uniform base case is 100 km^2 , resulting in an emissions rate scaling factor of $100/0.01 = 10,000$.

Each simulation was run for a total of 6 hours beginning at 9:00 AM LT and ending at 3:00 PM LT. The first hour of each simulation allows spin up and development of the PBL. Afterward, emissions occur at a constant rate for the remainder of each simulation.

4.2 Results

Maybe a little summary of what the sub-sections are here before launching into results?

4.2.1 Ozone cross sections

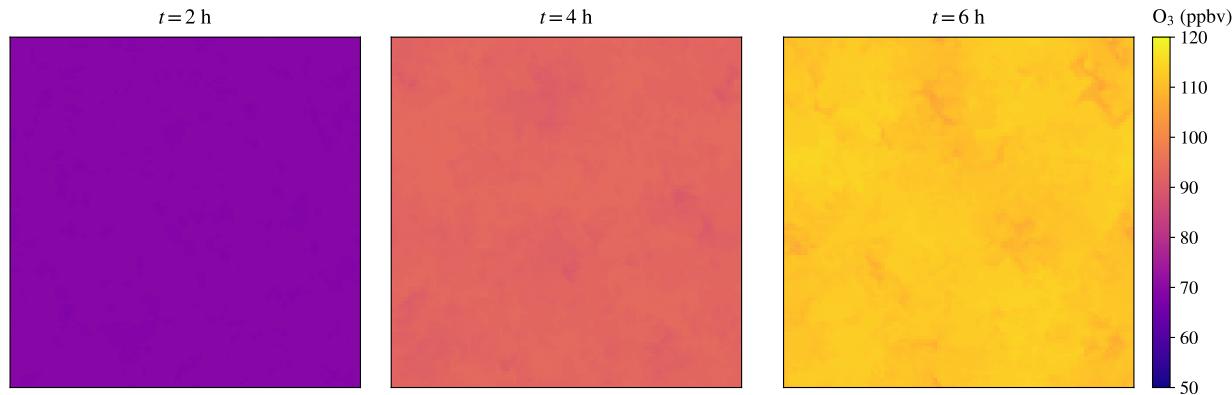


Figure 4.2: Ozone cross sections in the x-y plane at 2 hour intervals in the middle of the PBL ($z \sim 500 \text{ m}$) for the uniform base case.

In order to visualize the spatial heterogeneities present in ozone throughout each simulation, cross sections of ozone concentrations in the x-y plane were plotted for each emissions scenario. Cross sections were selected at a vertical level corresponding to the approximate middle of the PBL ($z \sim 500 \text{ m}$) and were plotted at regular, 2 hour intervals.

Ozone cross section plots for the uniform base case are shown in Figure 4.2. Ozone concentrations are displayed as molar fractions in parts per billion by volume (ppbv). Throughout each snapshot, the distribution of ozone is shown to be nearly uniform with minimal concentration gradients. Ozone concentrations steadily increase throughout the course of the simulation, reaching in excess of 110 ppbv by $t = 6 \text{ h}$.

Ozone cross sections for emission scenarios 1–3 are shown in Figures 4.3–4.5, respectively. By $t = 2 \text{ h}$, ozone concentrations have risen from their initial condition of 50 ppbv to a nearly uniform 60 ppbv in areas distant from the region where the emissions plume passes through. Approaching the area surrounding the plume, ozone concentrations are lower at $\sim 50 \text{ ppbv}$, indicating that very little ozone production occurs in the immediate vicinity of the emissions plume. This trend increases moving from emissions scenario 1 (Figure 4.3) to emissions scenario 3 (Figure 4.5), where the absence of elevated ozone levels in the central region of the plume is clearly visible.

By $t = 4 \text{ h}$ and $t = 6 \text{ h}$, ozone concentrations have risen in the region immediately surrounding the plume, reaching upwards of 110 ppbv in each scenario by $t = 6 \text{ h}$. The region of most efficient ozone production clearly overlaps with the region where the plume is rising through the PBL; however, for the highest spatial

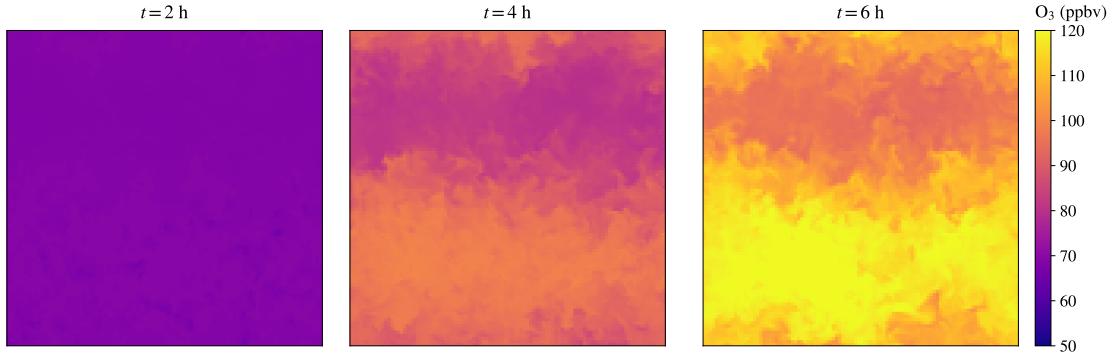


Figure 4.3: Ozone cross sections in the x-y plane at 2 hour intervals in the middle of the PBL ($z \sim 500$ m) for emissions scenario 1.

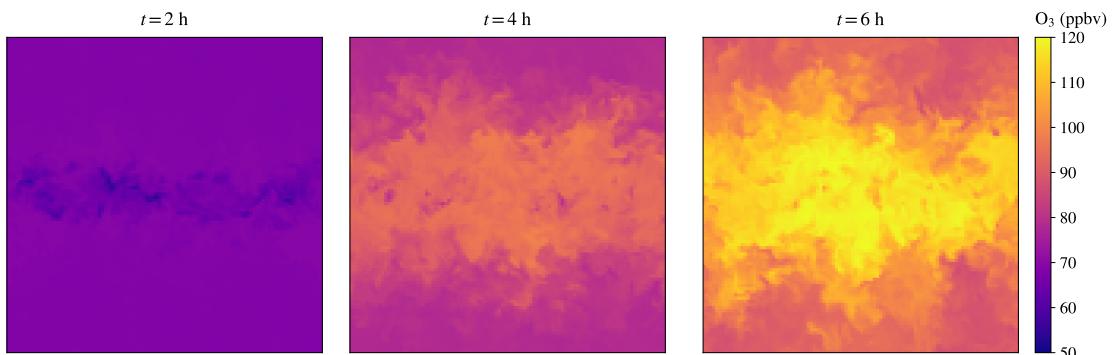


Figure 4.4: Ozone cross sections in the x-y plane at 2 hour intervals in the middle of the PBL ($z \sim 500$ m) for emissions scenario 2.

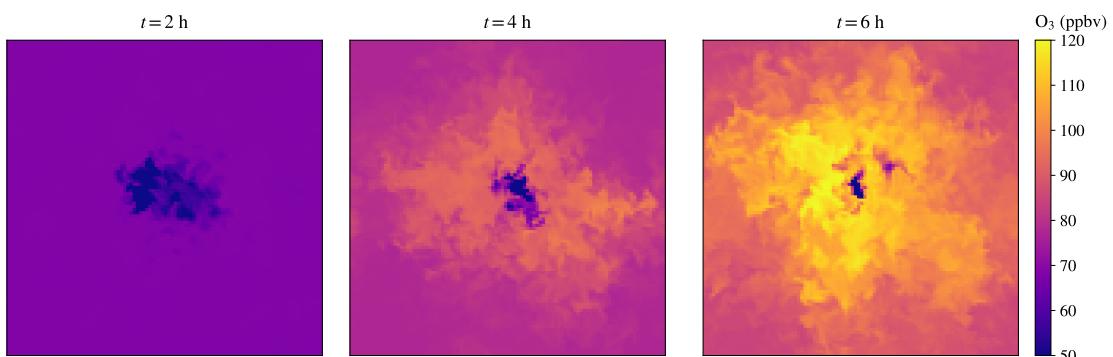


Figure 4.5: Ozone cross sections in the x-y plane at 2 hour intervals in the middle of the PBL ($z \sim 500$ m) for emissions scenario 3.

heterogeneity emissions scenario, scenario 3 (Figure 4.5), we find that ozone concentrations are significantly depressed in the immediate vicinity of the plume. This points to the non-linear nature of ozone production and its dependence on the relative abundance of NO_x and VOCs.

4.2.2 Spatio-temporal trends in ozone and its precursors

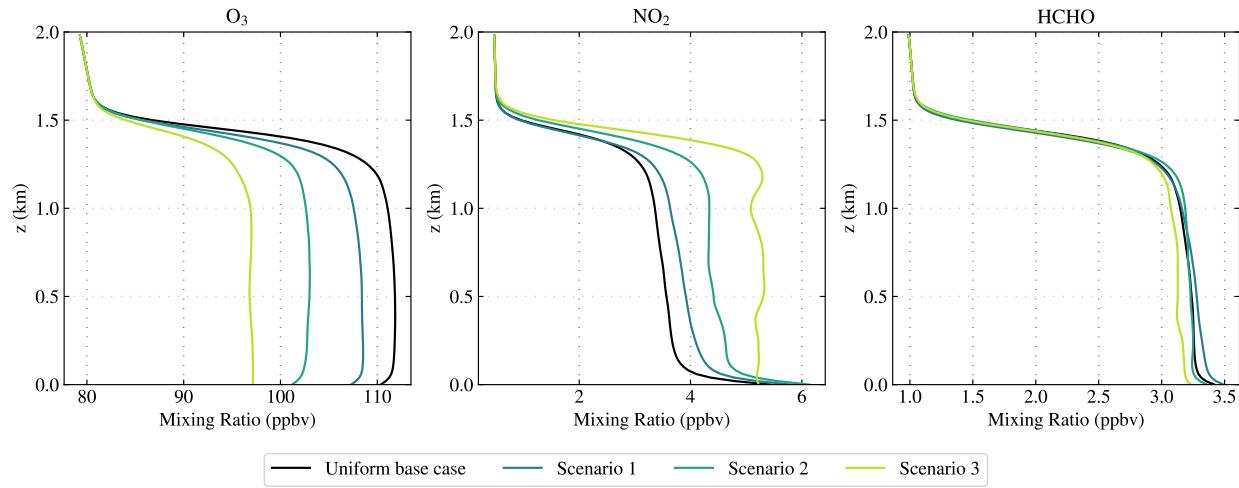


Figure 4.6: Vertical profiles at $t = 6$ h for ozone, NO_2 , and HCHO (left to right) for each emissions scenario. Each vertical profile indicates the species mean concentration when horizontally averaged at each vertical level.

Vertical profiles at $t = 6$ h for ozone, NO_2 , and HCHO (formaldehyde) across each emissions scenario are shown in Figure 4.6. For each plot, the vertical profile was computed by determining the horizontal average across the domain of each compound and for each vertical level. NO_2 is displayed alongside ozone to evaluate whether NO_x titration is occurring—at high NO concentrations, there is a net conversion of ozone to NO_2 via



Usually this reaction is balanced by photolysis of NO_2 , however, in emissions plumes with high concentrations of NO, Reaction 4.1 results in a net conversion of ozone to NO_2 . HCHO is chosen as a representative VOC.

We find that mean ozone concentrations are nearly uniform in the PBL for each emissions scenario, with a reduction in mean concentrations from ~ 112 ppbv in the uniform base case to ~ 97 ppbv for emissions scenario 3. By $t = 6$ h, the boundary layer height has grown to nearly $z = 1.5$ km, above which point ozone concentrations are nearly identical at ~ 80 ppbv across emissions scenarios. Note the initial condition for ozone is a uniform 50 ppbv throughout the entire domain, indicating that in the absence of additional NO_x and VOC precursors due to emissions, ozone concentrations rise by approximately 30 ppbv over 6 hours due to ambient precursor concentrations and photolysis reactions.

NO_2 concentrations vary considerably within the boundary layer, with concentrations approaching 6 ppbv

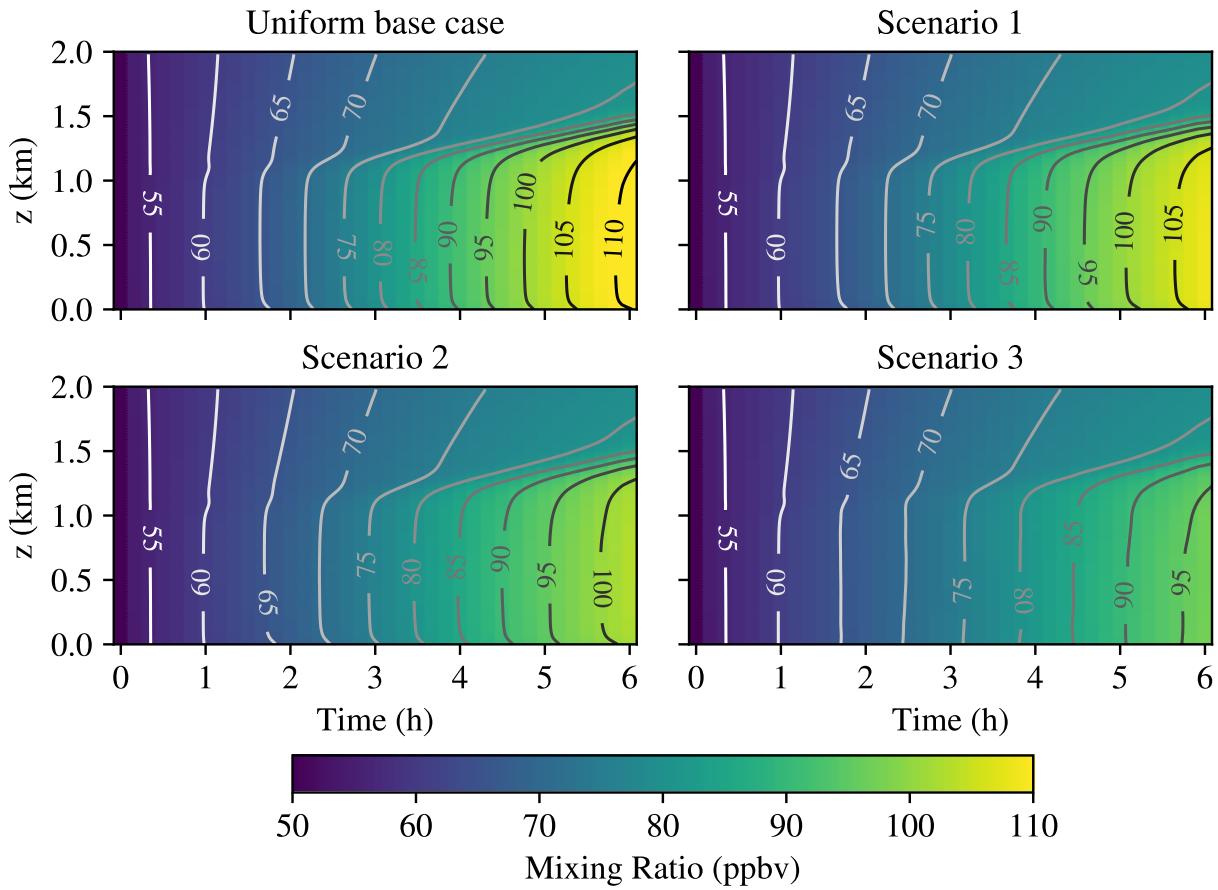


Figure 4.7: Ozone concentration time-height plots for each emissions scenario.

near the surface followed by a slightly decreasing trend in the middle to upper PBL. We find higher NO₂ concentrations as we move from the uniform base case to higher emissions spatial heterogeneity scenarios. We also find that under the highest emissions *SH* scenarios (scenario 2 and 3), the profile of NO₂ is more variable with height. The horizontal averaging likely hides a good portion of this variability, however concentration fluctuations suggest greater heterogeneity - could plot std dev?.

HCHO concentrations are relatively uniform across each emissions heterogeneity scenario, with concentrations between 3–3.5 ppbv in the PBL. Agreement in the abundance of HCHO across emission scenarios suggest that it is not as sensitive to emissions spatial heterogeneity as NO_x probably owing to the rate at which it reacts with other species.

edit this to be accurate for updated plot Time-height sections of ozone concentrations are shown for the uniform base case in Figure ?? and for emissions scenarios 1–3 in Figures ??–???. For each time-height figure, the horizontal average concentration of ozone was computed for each vertical level and at time in

the simulation output. Isopleths are superimposed on each time-height plot and indicate regions of constant ozone concentrations in increments of 5 ppbv.

During the first hour of each simulation, ozone concentrations gradually increase nearly uniformly from the initial concentration of 50 ppbv to 60 ppbv. Emissions are turned on at $t = 1$ h, however ozone concentrations for emissions scenarios 1–3 do not appear to appreciably diverge from the uniform base case until $t \simeq 2$ h and beyond. After this point, ozone concentrations increase in the PBL of each scenario (the PBL height gradually grows throughout the simulation as indicated by the region of highest ozone concentrations due to the constant heat flux at the surface). Ozone concentrations alongside the ozone formation rate are highest in the uniform base case (Figure ??). Note that between hours 5 and 6, ozone concentrations in the PBL increase by approximately 10 ppbv as indicated by isopleths. By comparison, ozone concentrations increase by approximately 5 ppbv for scenario 3 (Figure ??) during the same time period.

To quantify the relative difference between ozone production in the uniform base case and each emission scenario, Figures ??–?? are time-height plots for scenarios 1–3 where the percent difference between ozone in the uniform base case and each scenario is displayed with superimposed isopleths. Percent difference is calculated as

$$\% \text{ difference} = 100 \times \left(\frac{\overline{[O_3]}(t, z)_{\text{Scenario}} - \overline{[O_3]}(t, z)_{\text{Base case}}}{\overline{[O_3]}(t, z)_{\text{Base case}}} \right), \quad (4.2)$$

where $\overline{[O_3]}(t, z)_{\text{Scenario}}$ is the horizontally averaged concentration of ozone at time t and vertical level z for a particular scenario and $\overline{[O_3]}(t, z)_{\text{Base case}}$ is the horizontally averaged concentration of ozone at time t and vertical level z for the uniform base case.

Figure ?? shows percent difference of ozone concentrations for scenario 1. Regions shaded in blue indicate negative percent difference (i.e., the uniform base case contains higher concentrations in a given region) while red indicates positive percent difference. Regions shaded in gray indicate zero percent difference. We find that ozone concentrations for emissions scenario 1 are in good agreement with the uniform base case within the free troposphere during the entire simulation and also in the PBL prior to ~ 2 hours. After this point, ozone concentrations are up to 3% less in the PBL through $t = 6$ h.

We find similar but heightened trends for ozone concentration percent difference in Figures ?? and ?? for emissions scenarios 2 and 3, respectively. For scenario 2, ozone concentrations are up to 8% less in the PBL through $t = 6$ h and are reduced by up to $\sim 13\%$ for scenario 3.

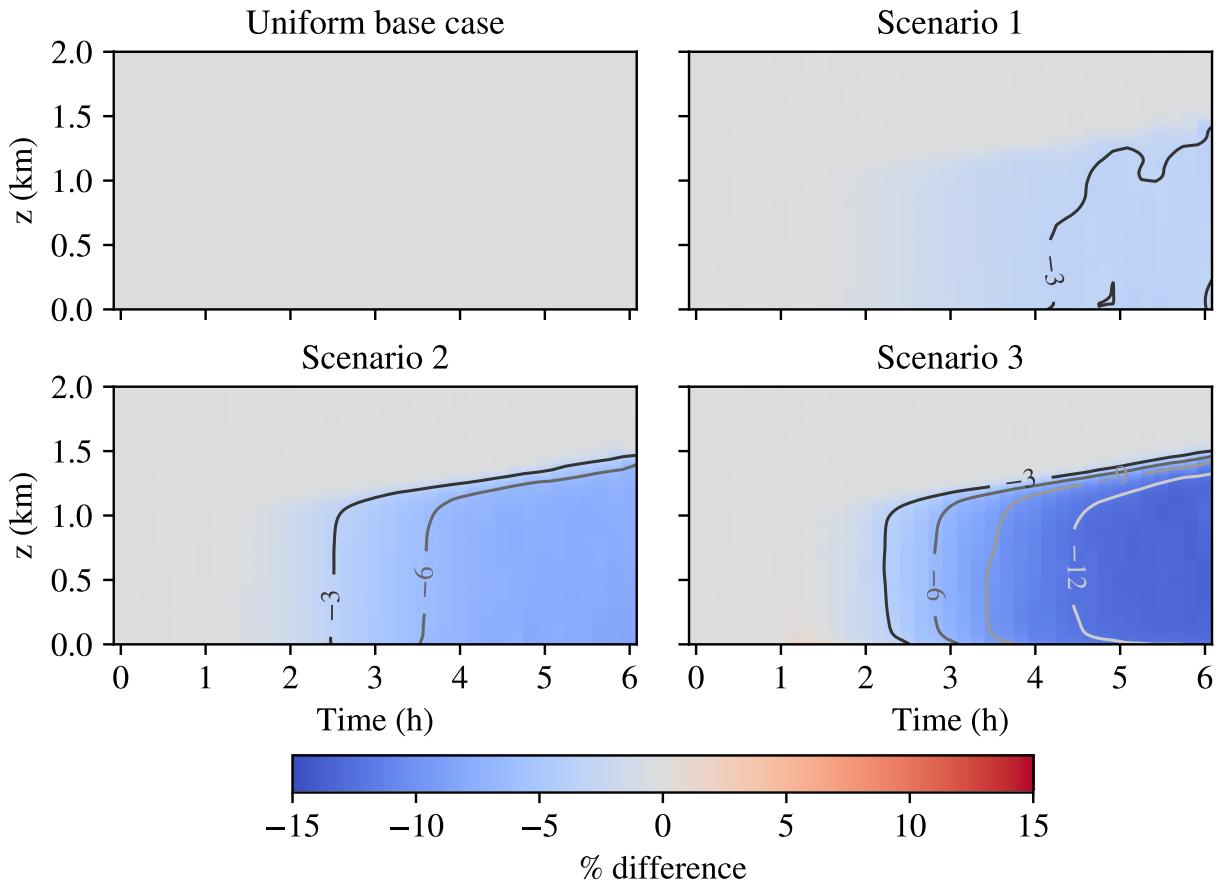


Figure 4.8: Time-height plots of ozone percent difference for each emissions scenario.

4.2.3 Spatial heterogeneity in the atmosphere of ozone and its precursors

In addition to the spatial heterogeneity of each emission pattern as shown in Figure 4.1, once gas phase species are emitted from the surface, their atmospheric distribution will be influenced by the emissions pattern heterogeneity, the strength of mixing, and chemical reactions that alter the abundance of compounds. We refer to the spatial heterogeneity of a gas phase species in the atmosphere as the species' *field* spatial heterogeneity.

Figure 4.9 shows time-height plots of the field spatial heterogeneity for NO (top), HCHO (middle), and ozone (bottom) for the uniform base case. Field SH is computed for horizontal cross sections of the domain at each vertical level and each time. Regions filled with dark blue correspond to low field SH while regions in green and yellow indicate high field SH . In Figure 4.9, the field SH of each compound is very low. After $t = 1$ h, NO field SH is ~ 0.01 within the PBL. HCHO field SH is ~ 0.001 within the PBL following the release of emissions at $t = 1$ h, with slightly higher values of 0.01 near the upper PBL developing after $t = 2$

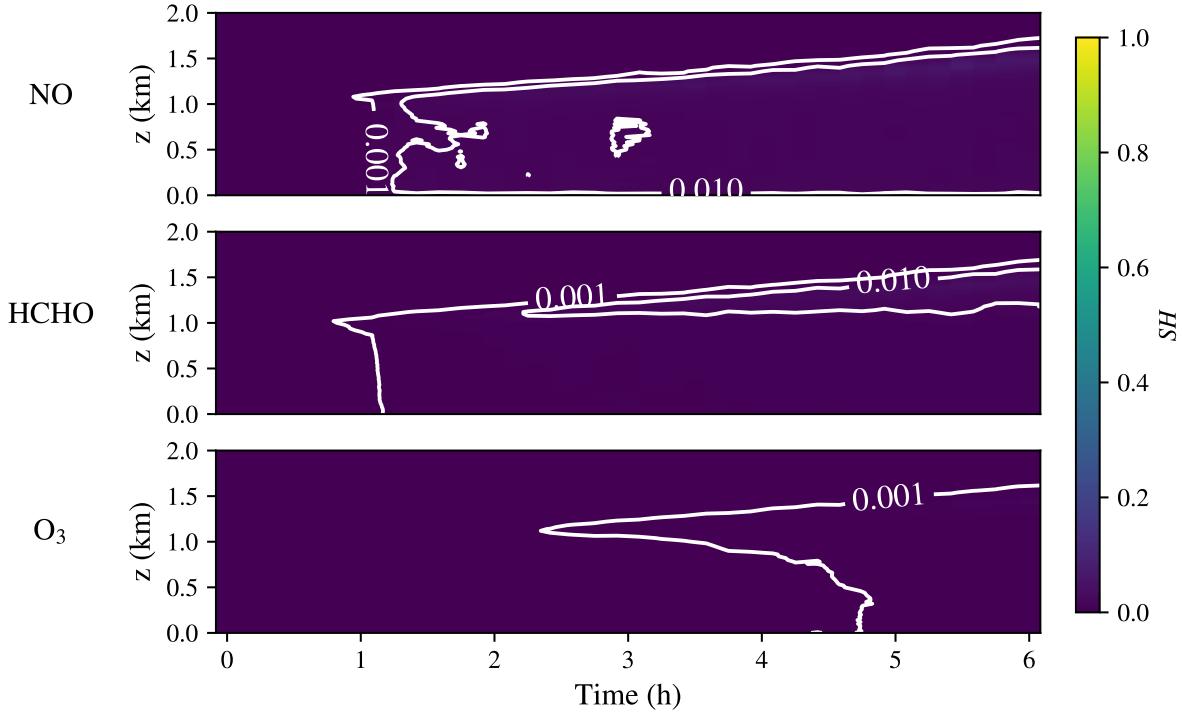


Figure 4.9: Time-height plot of field SH for O_3 , NO_x , and $HCHO$ in the uniform base case. SH value contours are shown in grayscale for each subplot.

h. Ozone field SH is the lowest of the three compounds, with values of 0.001 developing in the upper PBL after $t = 2$ h and extending to the surface by $t = 5$ h.

Similarly, Figure 4.10 shows time-height plots for ozone and its precursors for emissions scenario 1. Recall that the emissions SH for scenario 1 is 0.33. Field SH for all species is lower than the emissions SH (as we expect due to atmospheric processes that disperse, dilute, and alter the concentration of each compound). As emissions begin at $t = 1$ h, the field SH of NO is ~ 0.1 within the PBL and increases to 0.2 after approximately 2 hours. Around $t = 5$ h, the field SH of NO decreases back down to 0.1 within the PBL. Following the release of emissions at $t = 1$ h, HCHO field SH is 0.05, increasing to 0.1 by approximately 2 hours and 30 minutes where it remains for the duration of the simulation. Similar to field SH for the uniform base case, ozone exhibits the lowest field SH of all three species, with values of 0.001 from $t = 1$ h to $t = 3$, afterward increasing to 0.01.

We find similar trends to scenario 1 in the field SH of ozone and its precursors for emissions scenario 2 as shown in Figure 4.11. Recalling that the emissions SH of scenario 2 is 0.60, we find that the field SH of NO and HCHO correspondingly increase compared to scenario 1. Following emissions at $t = 1$ h, the field

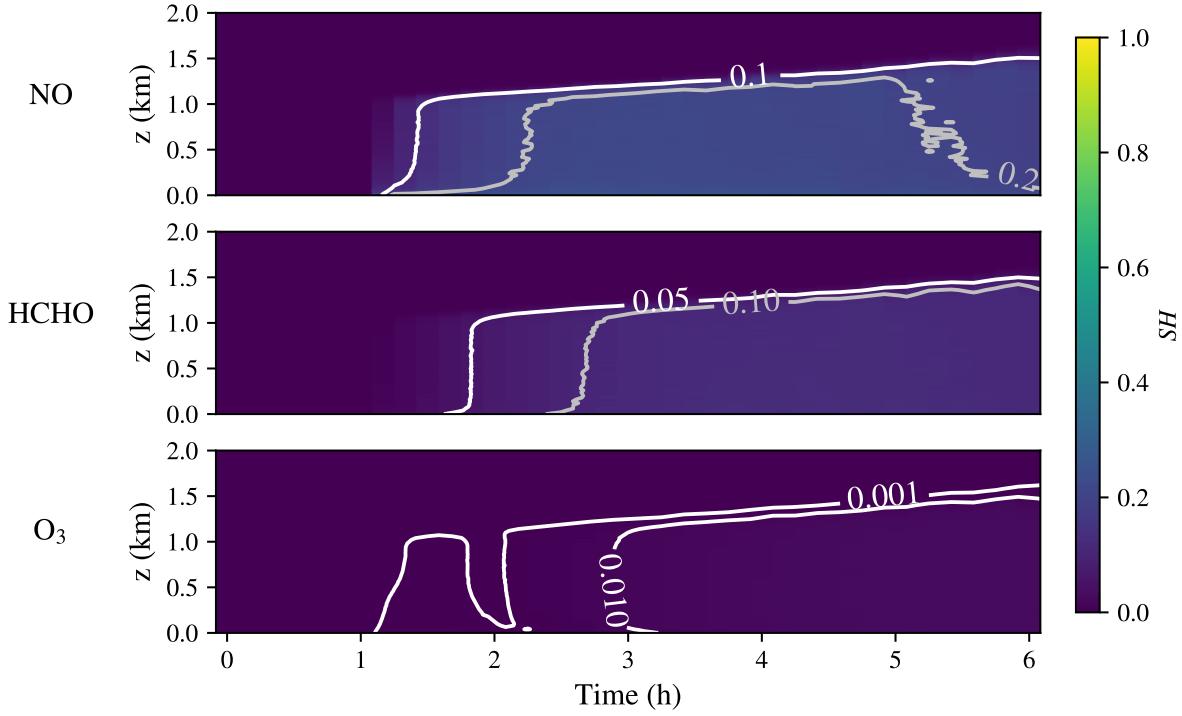


Figure 4.10: Time-height plot of field SH for O_3 , NO_x , and $HCHO$ in emissions scenario 1. SH value contours are shown in grayscale for each subplot.

SH of NO in the PBL increases to 0.3 over nearly the entire height PBL except for near the surface where the field SH reaches 0.4. The field SH of HCHO increases to 0.15 by $t = 3$ h, where it remains through the duration of the simulation. The pattern of field SH for ozone closely matches its behavior noted for scenario 1—from $t = 1$ h to $t = 3$ h, ozone field SH is of order 0.001, increasing to 0.01 afterwards.

Figure 4.12 shows the field SH of ozone and its precursors for emissions scenario 3. Scenario 3 posses the highest emissions spatial heterogeneity, $SH = 1$. As a result, the field SH of both NO and HCHO are markedly higher compared to previous scenarios. Field SH of NO varies both spatially and temporally for scenario 3. Following the release of emissions at $t = 1$ h, we find a high field SH of 0.8 near the surface that persists for the duration of the simulation. Moving up in the PBL, field SH ranges from 0.4 to 0.6. From $t = 1$ h to $t = 2$ h, the region of high field SH at 0.6 is localized near the surface. Following this point, this high field SH region extends upwards to the top of the PBL from $t = 2$ h to $t = 3$ h. After this point, field SH lowers back down to 0.4 over most of the PBL. Field SH of HCHO is relatively uniform through the PBL and increases following emissions to 0.2 by $t = 3$ h where it remains for the duration of the simulation. Similar to the field SH of ozone discussed for scenarios 1 and 2, ozone exhibits a very similar pattern for scenario

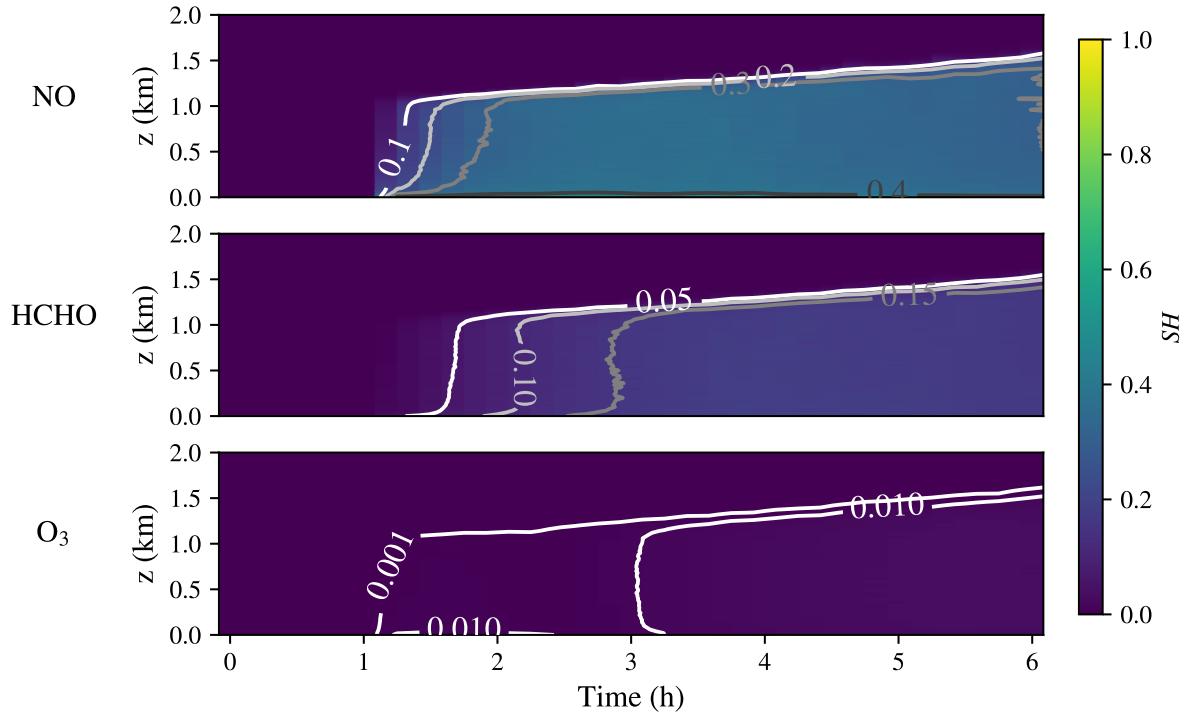


Figure 4.11: Time-height plot of field SH for O_3 , NO_x , and $HCHO$ in emissions scenario 2. SH value contours are shown in grayscale for each subplot.

3–from $t = 1$ h to $t = 3.5$ h, ozone field SH is of order 0.001, increasing to 0.01 afterwards.

Decrease in NO field sh seems to occur around the same time that HCHO field sh increases, shortly followed by ozone. My theory is that this may point to changes in ozone production efficiency as the relative abundance of NO_x changes due to continued emissions and perhaps the VOCs are reacting more to produce more ozone (thus increasing the conc. and coupling the field sh of ozone to VOC field sh?) Its also the case that there ARE aerosols in these simulations and that presents an important pathway for the removal of NO_x via nitric acid to form aerosol nitrate and nitric acid deposition.

4.3 Discussion

This either goes here or in the introduction..

- Worth noting at some point past studies that have evaluated the production of ozone in LES as well as some studies that investigate the impacts of spatial het. on ozone production (Initial studies investigated idealized interactions between turbulence and ozone chemistry in the PBL, more recent studies have branched into region-specific studies to investigate impacts of spatially heterogeneous emissions and

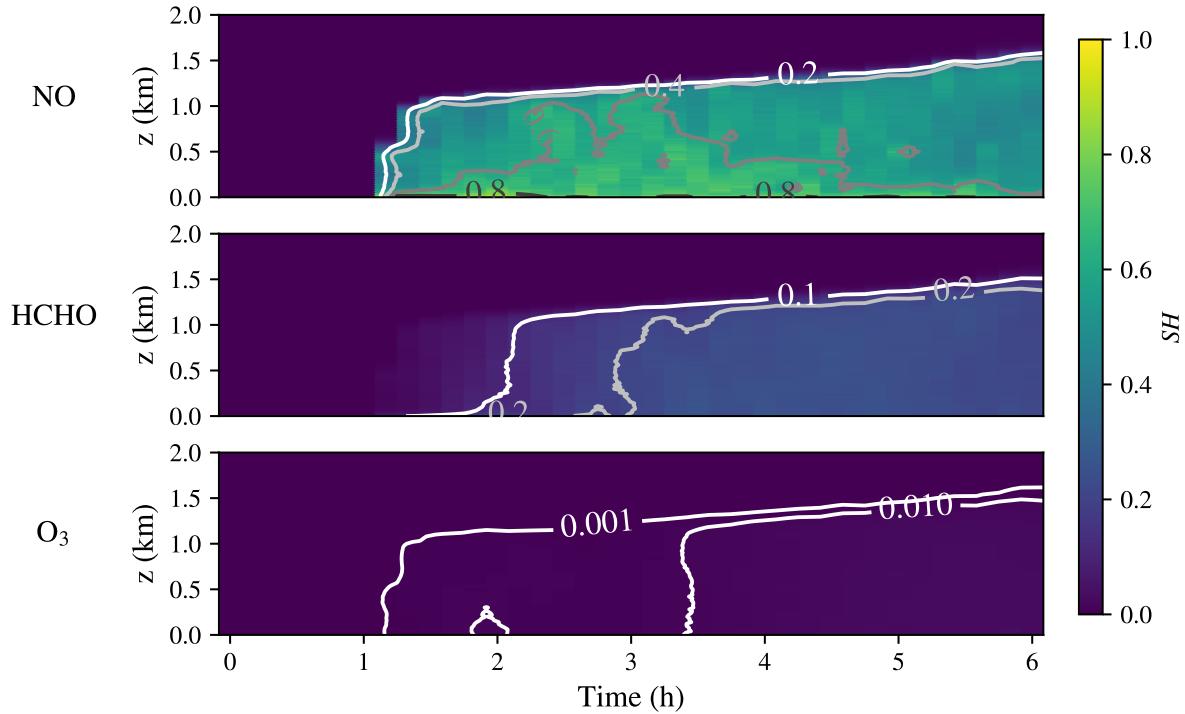


Figure 4.12: Time-height plot of field SH for O_3 , NO_x , and $HCHO$ in emissions scenario 3. SH value contours are shown in grayscale for each subplot.

turbulence-chemistry interactions on local ozone production).

- Schumann 1989 Idealized LES of boundary layer - investigate binary reactions (such as those typical of ozone production) with varying reaction rates. For rates typical of ozone-nox reactions, the mechanism is significantly impacted by turbulence.
- Sykes et al. 1992 Idealized LES of boundary layer - investigate turbulence chemistry interactions on ozone chemistry, particularly focused on the removal mechanism oxidizing NO to $NO_2 + O_2$. Find that the production rate of NO_2 is highly dependent on the turbulent mixing of the plume. They show that the turbulence segregation coefficient can be approximated as uniform in a emitted plume.
- Auger and Legras 2007 (seems very similar to what I am doing here) LES of PBL over 10×10 km domain. Indicate that segregation is strongest in the first two hours - after 3 hours segregation is largely reduced due to efficient mixing in the PBL.
- Zhong, Cai, and Bloss 2015 Similar to Zhong et al 2017, find that ozone production rate is reduced due to incomplete mixing.

- Zhong, Cai, and Bloss [2017](#) LES study of O₃-NO_x-VOC chemistry in urban street canyons characterized by high spatial variability in concentration gradients. NO_x and HO_x radicals were consumed to produce NO₂ and O₃. Segregation effect due to incomplete mixing reduces the production of NO₂.
- Y. Wang, Ma, Muñoz-Esparza, Li, et al. [2021](#)
- Y. Wang, Brasseur, and T. Wang [2022](#) Similar to wang 2023
- Y. Wang, Ma, Muñoz-Esparza, Dai, et al. [2023](#) Use of LES (WRF-Chem LES [what chem mechanism?](#)) for urban (Hong Kong) emissions compared against mesoscale simulations, show that NO_x is underestimated and O₃ overestimated in mesoscale simulations when compared to LES, attributed to the higher spatial resolution of emissions and explicitly resolving turbulent transport.

Chapter 5

Impacts of emissions spatial heterogeneity on aerosol properties and CCN activity

5.1 Ideal coagulation runs

5.2 Full multiphase chemistry runs

5.2.1 aerosol size distributions

- Number dist render
- Mass dist render

5.2.2 aerosol composition

- Time-height plots for sulfate, nitrate, ammonium
- % mass fraction vs particle diameter plots
- kappa distributions (either here or in the ccn subsection?) render

5.2.3 aerosol mixing state

- Vertical profile of average particle χ, D_α, D_γ
- Vertical profile of ccn χ, D_α, D_γ

5.2.4 ccn

- Vertical profile of ccn conc at each supersaturation level

- Vertical profile of ccn χ , D_α , D_γ
- time height plots of ccn % error
- (potentially) some sort of box plot ccn error thing similar to what I showed at IAMA?

5.2.5 Runs without ammonia

- Vertical profile of SNA
- Vertical profile of ccn conc at each supersaturation level

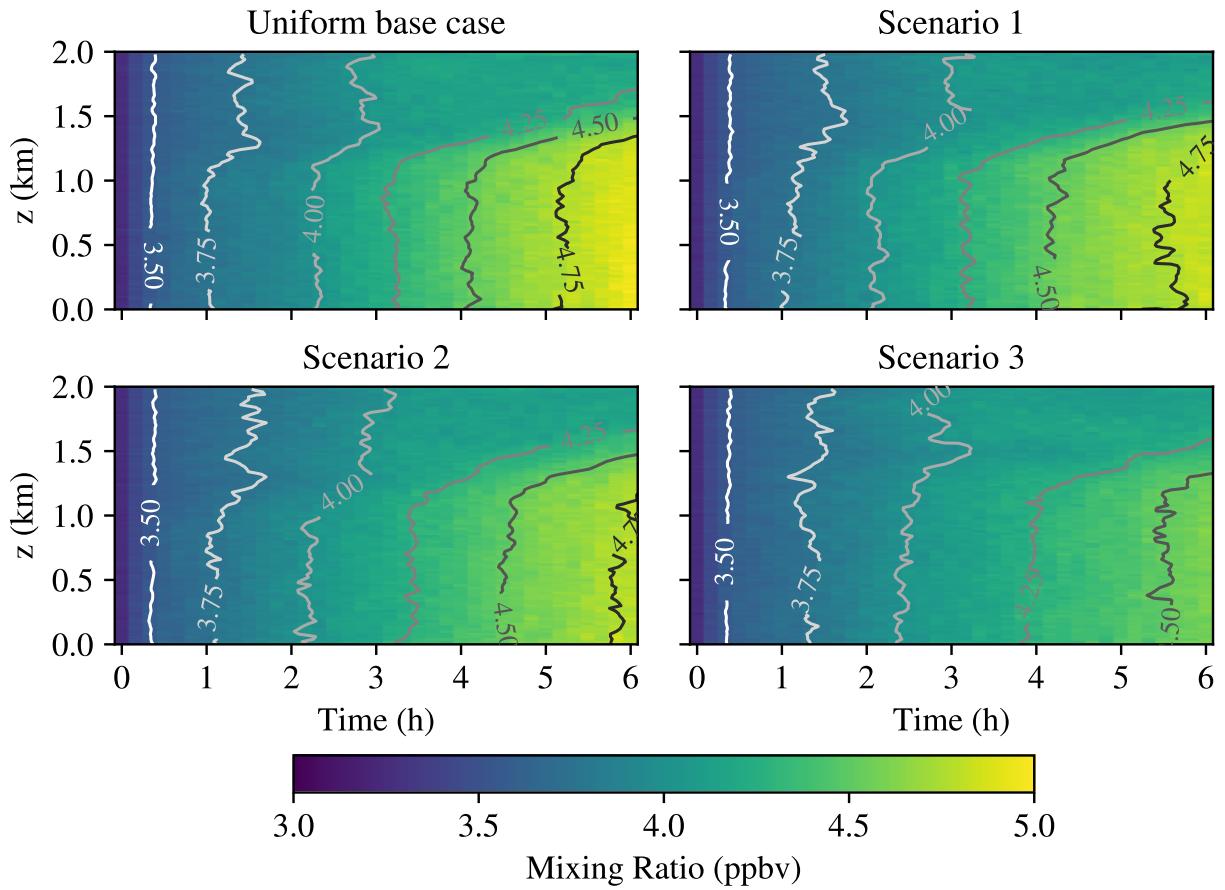


Figure 5.1: Sulfate

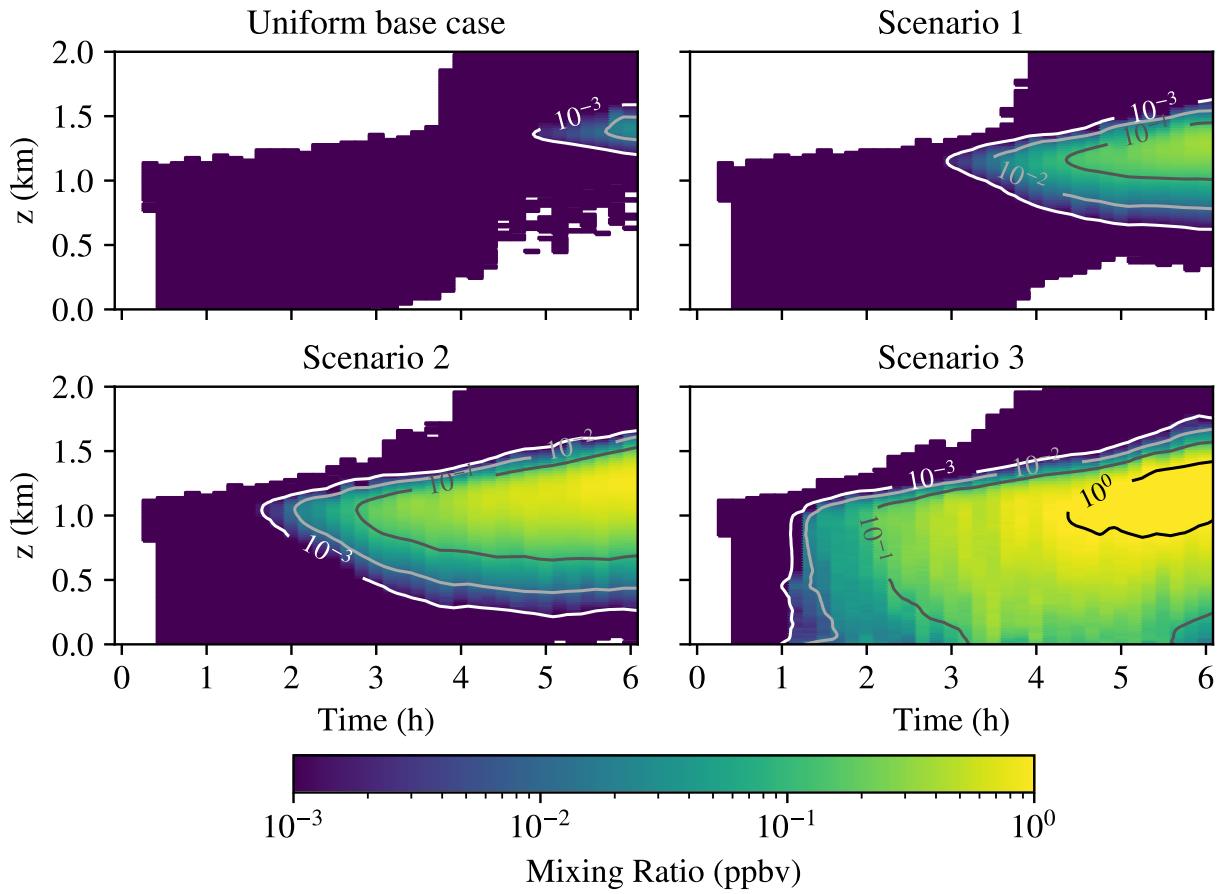


Figure 5.2: Nitrate

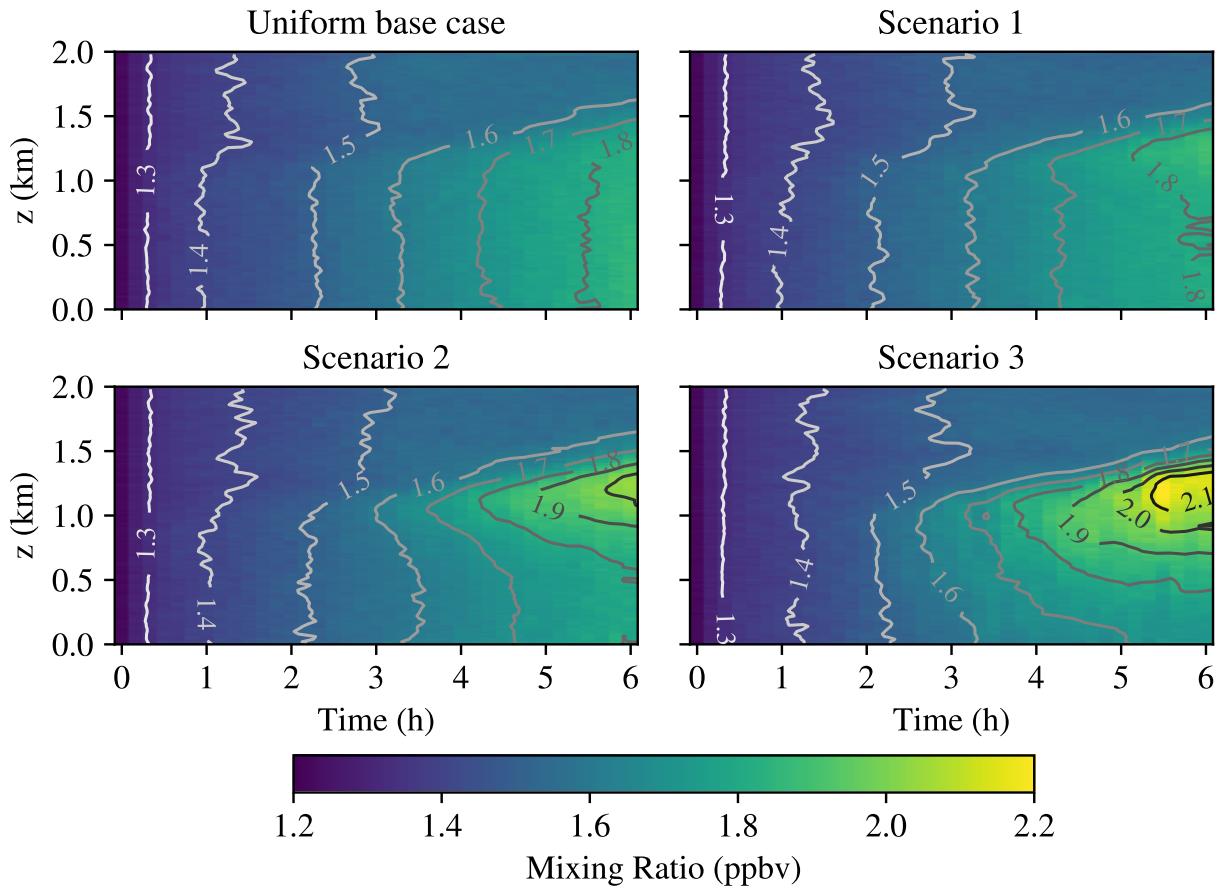


Figure 5.3: Ammonium

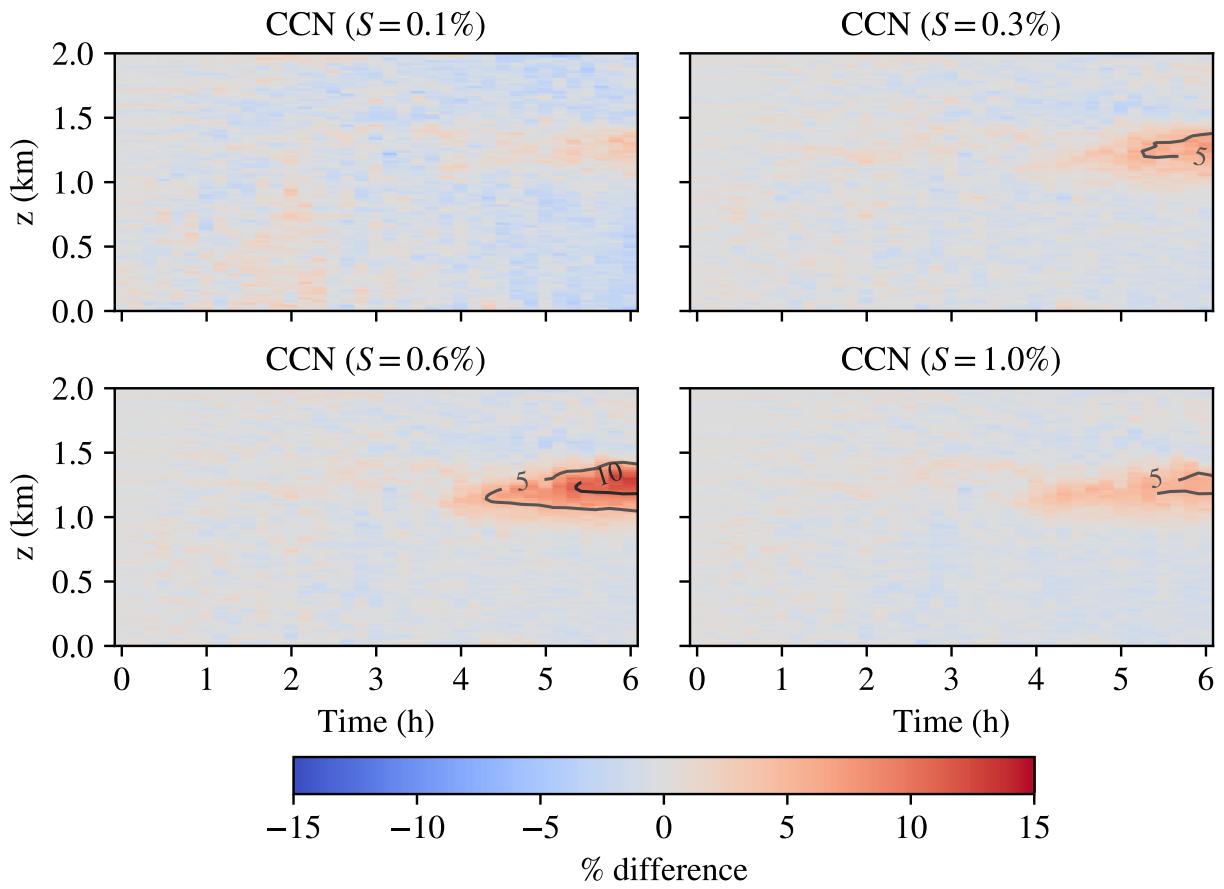


Figure 5.4: Scenario 1

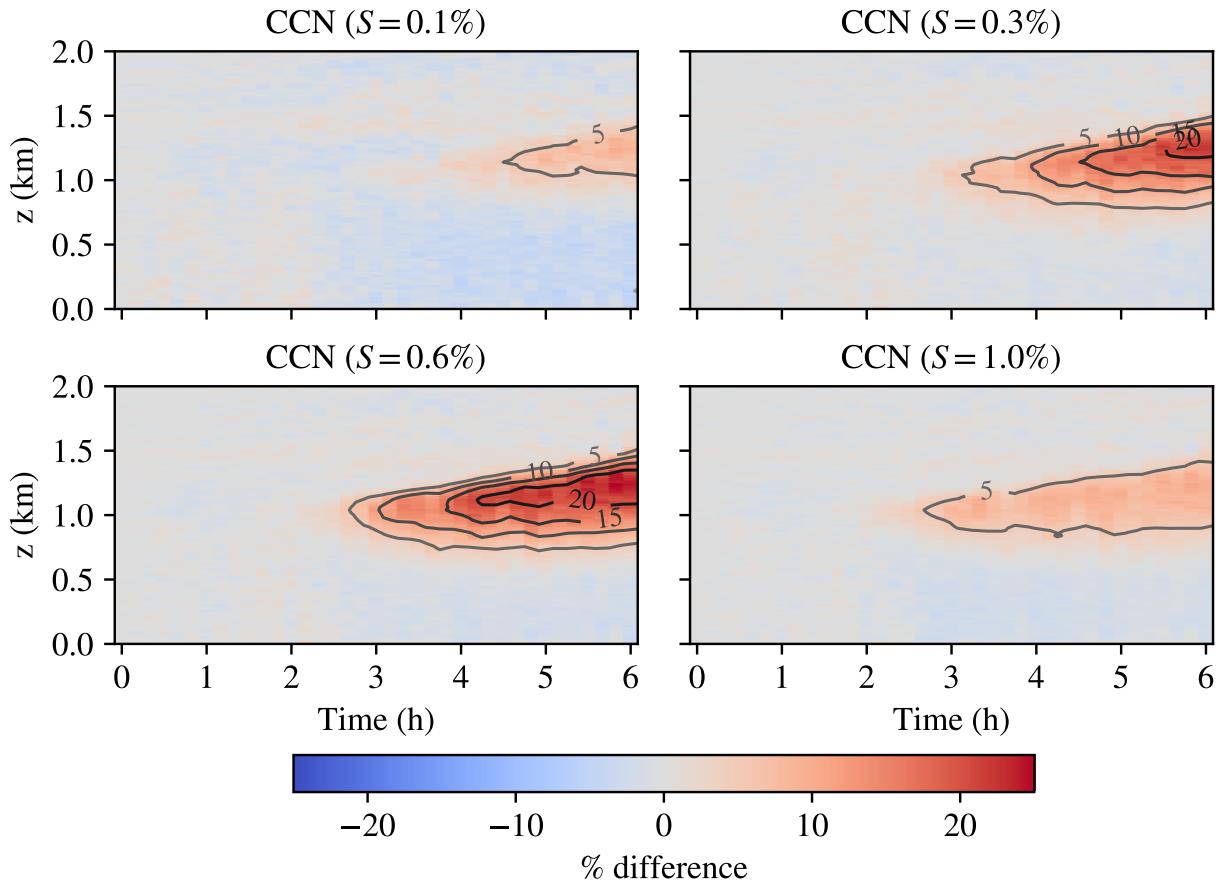


Figure 5.5: Scenario 2

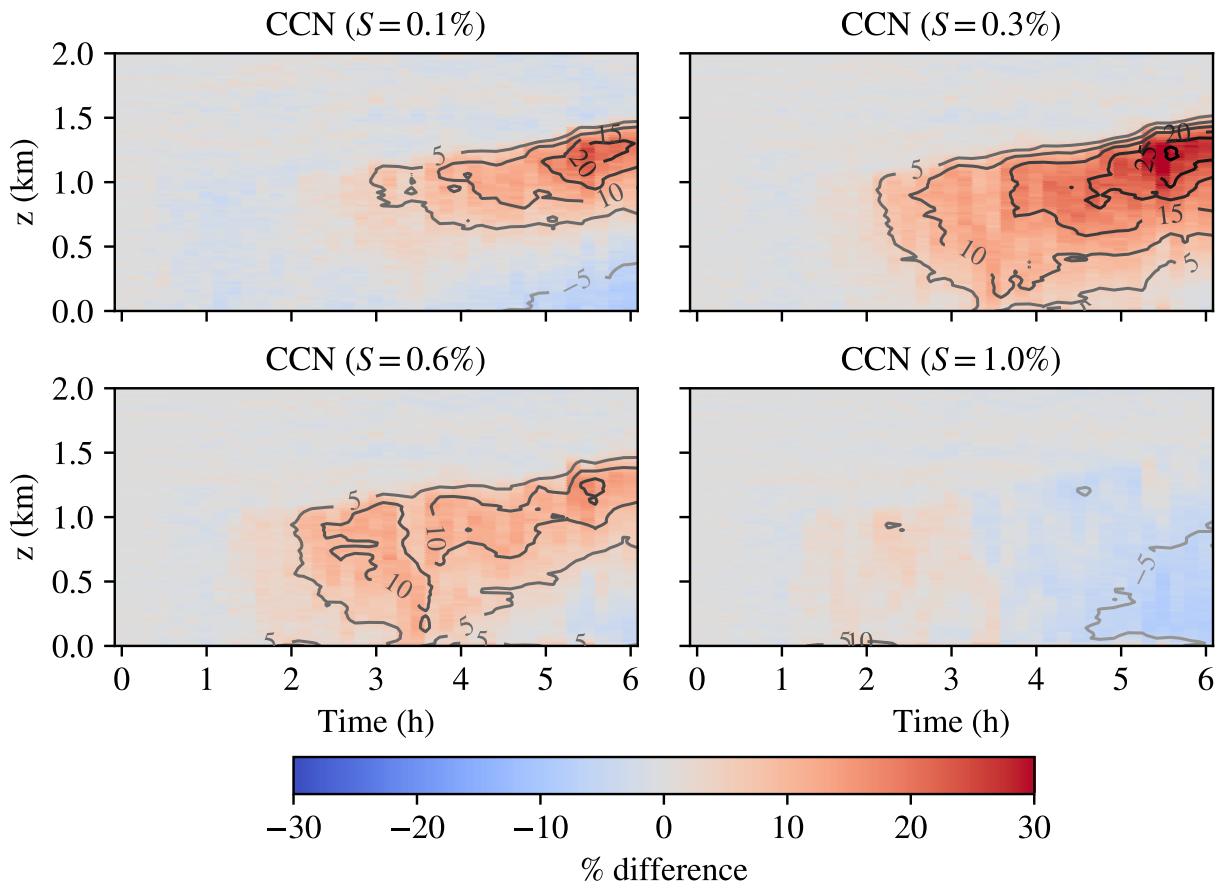


Figure 5.6: Scenario 3

Chapter 6

Conclusions

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