Chemical Transport of Neutral Atmospheric Constituents by Waves and Turbulence: Theory and Observations

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1. Introduction

The vertical transport of atmospheric constituents by waves and turbulence has a profound impact on the chemistry and composition of the atmosphere below the turbopause [e.g., Walterscheid, 1981; Walterscheid and Schubert, 1989; Xu et al., 2003; Zhu et al., 2010; Gardner and Liu, 2010]. In the steady state, the net chemical production and loss of a species is balanced by its vertical transport. Most atmospheric modeling studies focus on eddy transport by turbulent mixing, which is modeled as a larger-scale analog of molecular diffusion [e.g., Garcia and Solomon, 1994; Marsh et al., 2007; Garcia et al., 2014]. However, it has been shown that other transport processes, which are nondiffusive in character, also play important roles and can transport constituents against the diffusive tendency. Chemical transport arises when the density fluctuations of a chemically active species, caused by wave- and turbulence-induced perturbations of its chemistry, are strongly correlated with the vertical wind fluctuations. Strobel [1981, 1989] generalized the diffusion equation to account for chemistry and showed that strong coupling of chemistry and temperature through the reaction rates gives rise to an additional turbulence-induced flux that is not proportional to the gradient of the species mixing ratio. Garcia and Solomon [1985] used a gravity wave parameterization scheme to express the chemical transport in terms of a linearized chemical loss coefficient and vertical wave number. Walterscheid and Schubert [1989] showed that monochromatic wave perturbations of chemistry induce significant vertical fluxes of mesospheric O₃ and OH. We reported similar results for the measured nighttime chemical flux of mesospheric Na [Gardner and Liu, 2010]. In addition, dissipating waves impart a downward velocity to the atmosphere that is proportional to the heat transport velocity and is the same for all species. This mechanism is called dynamical transport to distinguish it from eddy and chemical transport. In the mesopause region all of these mechanisms make important contributions to the vertical transport of atmospheric constituents.

The significance of these additional transport mechanisms is best illustrated by recent attempts to model the mesospheric Na and Fe layers with the Whole Atmosphere Community Climate Model (WACCM) [Marsh et al., 2013; Feng et al., 2013]. These metals are injected into the lower thermosphere and upper mesosphere by meteoric ablation and are then transported downward to chemical sinks below about 85 km. The meteoric influx is balanced by downward transport, which determines the densities of the species. If the influx is increased or the transport velocity decreased, then the density will increase proportionally [Plane, 2004].
Vertical transport is modeled in WACCM, primarily as an eddy mixing process, which is characterized by the eddy diffusivity \cite{Garcia et al., 2007}. \textit{Marsh et al.} [2013] and \textit{Feng et al.} [2013] were able to reproduce the global distribution of Na and Fe with good fidelity by employing a global mean influx of \(\sim 2000\) Na atoms/cm\(^2\)/s and \(\sim 7000\) Fe atoms/cm\(^2\)/s. However, nighttime lidar measurements of vertical fluxes of Na and Fe show that the fluxes are much larger, viz., \(\sim 17,000 \pm 3000\) Na atoms/cm\(^2\)/s and \(\sim 100,000 \pm 20,000\) Fe atoms/cm\(^2\)/s \cite{Gardner et al., 2014; Huang et al., 2014}. This discrepancy suggests that vertical constituent transport as modeled by WACCM is too slow, at least for Na and Fe in the mesopause region. Of course, there are also uncertainties in the lidar observations, which are discussed in section 4. The transport problem is not unique to WACCM. Modelers can compensate for deficiencies in the way vertical transport is calculated and still produce realistic density profiles of the metal layers, by simply adjusting the meteoric influx, which is itself an uncertain quantity \cite{Plane, 2012}. During the past several decades, the values of the eddy diffusivity \((k_{eddy})\) and meteoric influx used to model lidar and satellite observations of the metal layers have varied by as much as a factor of 10 \cite[e.g., Gardner and Liu, 2007]{Gardner and Liu, 2007}.

In this paper we derive a solution to the continuity equation for chemically active species, which is then used to derive explicit formulas for the vertical chemical fluxes induced by waves and turbulence. The theory is compared with the wave-induced chemical fluxes of mesospheric Na and Fe measured at nighttime by Doppler lidars at the Starfire Optical Range, New Mexico, and the Table Mountain Lidar Facility, Colorado. We explore the wave- and turbulence-induced fluxes of mesospheric Na, Fe, and O\(_3\) and show that vertical chemical transport of these species is at least as significant as the other transport mechanisms, and in some cases it is the dominant process. We also show that chemical transport for the mesospheric metals and for O\(_3\) can vary considerably between night and day. Although vertical transport has only a minor influence on the steady state O\(_3\) densities, its influence on the mesospheric metals is substantial.

\section{2. Theory}

The density response of an atmospheric layer, composed of a neutral meteoric constituent \(C\), is governed by the continuity equation:

\begin{equation}
\frac{\partial \rho_C}{\partial t} + \nabla \cdot \left( \rho_C \mathbf{V} \right) = \mathbf{M}_C + \mathbf{P}_C - \mathbf{L}_C,
\end{equation}

where \(t\) is time, \(\rho_C\) is the density of \(C\), \(\mathbf{V}\) is its velocity, \(\mathbf{M}_C\) is its meteoric influx, and \(\mathbf{P}_C\) and \(\mathbf{L}_C\) are, respectively, the chemical production and loss rates of \(C\). For nonmeteoric species \(\mathbf{M}_C = 0\). We assume that the effects of molecular diffusion are negligible in comparison to the wind fluctuations so that the constituent velocity is equal to the atmospheric velocity. We also assume that the unperturbed wind and temperature fields and the constituent profiles are horizontally homogeneous so that the perturbed density profile may be written in the form

\begin{equation}
\rho_C(t; \mathbf{r}) = e^{-\chi(t) + \zeta} \rho_{C0}(z - \zeta).
\end{equation}

\(\mathbf{r} = x \hat{x} + y \hat{y} + z \hat{z}\) denotes the three-dimensional position vector where \(x\), \(y\) and \(z\) are, respectively, the zonal, meridional, and vertical coordinates. \(\rho_{C0}\) is the unperturbed density profile in the absence of wind fluctuations. This form for \(\rho_C\) has been shown to accurately describe the fluctuations of inert species and to provide good descriptions of the fluctuations for chemically active mesospheric Na and Fe \cite[e.g., Huang et al., 2013]{Huang et al.}.

Wind fluctuations distort the species profile in two ways. The multiplicative factor \(e^{-\chi(t) + \zeta}\), which is related to the divergence of the perturbed wind field \(\chi\) and to the perturbed chemical production and loss terms \(d\chi\), see equation (4) below), increases or decreases the density depending on the sign of \(\chi + d\chi\). The term \(\zeta\) represents the displacement of the atmosphere and species, caused by the vertical wind fluctuations. When the chemistry of a reactive species is perturbed by the wind fluctuations, the density of the species will be affected by its perturbed chemistry, but its vertical displacement and that of the background atmosphere will not. In other words, \(\zeta\) is identical to its value for inert species, while \(d\chi\) depends on the species chemistry.
The primary effect of the mean horizontal winds is advection, so we look for solutions to (1) of the form

\[ \zeta(t, t) = \zeta(x, y, z, t), \]
\[ \chi(t, t) = \chi(x, y, z, t), \]
\[ \delta_C(t, t) = \delta_C(x, y, z, t), \]

where \( u, v, \) and \( w \) denote the zonal, meridional, and vertical winds, and the overbars denote the mean values. By substituting (2) in (1) and applying (3), we obtain the following differential equations for \( \zeta, \chi, \) and \( \delta_C \)

\[ -\frac{\partial \zeta}{\partial t} + w + \nabla \cdot \mathbf{V} = 0 \]
\[ -\frac{\partial \chi}{\partial t} + v + \nabla \cdot \mathbf{V} = 0 \]
\[ -\frac{\partial \delta_C}{\partial t} + \nabla \cdot \mathbf{V} \delta_C = \frac{M_C + Q_C}{\rho_C} \]

where
\[ Q_C = P_C - L_C, \]

and the primes denote perturbed quantities. Equations (2)–(4) describe the constituent fluctuations in the Cartesian reference frame that is moving with the mean wind. Notice that \( \zeta \) and \( \chi \) depend only on the wind field. Only \( \delta_C \) depends on the species’ chemistry and its density profile.

For a minor species, the mixing ratio is defined as the species density divided by the total atmospheric density \( \rho_A \), which from (2) is given by

\[ \frac{\rho_C(z)}{\rho_A(z)} = \frac{e^{-(y + \delta_C)C_0(z - \zeta)}}{e^{-(y + \delta_C)C_0(z - \zeta)}} = e^{-\delta_C \rho_A(z - \zeta) / \rho_A(z - \zeta)}. \]

According to (4), \( \delta_C = 0 \) for inert nonmeteoric species. Therefore, if the mixing ratio profile is constant with altitude, from (5) we see that in the absence of chemistry, there will be no fluctuations in the species mixing ratio. In fact, by assuming this form for the mixing ratio, substituting it into the continuity equation

\[ \frac{\partial}{\partial z} \left( \frac{\rho_C}{\rho_A} \right) + \mathbf{V} \cdot \nabla \left( \frac{\rho_C}{\rho_A} \right) = \frac{M_C + P_C - L_C}{\rho_A}, \]

and then applying (3), it is not difficult to show that \( \zeta \) and \( \delta_C \) are indeed solutions to the partial differential equations given in (4).

We assume that the mean vertical wind and the divergence of the mean wind field are negligible and that the meteoric influx is independent of the gravity wave fluctuations. Furthermore, we note that in the steady state the constituent density is constant because the meteoric influx and the net chemical production and loss are balanced by vertical transport, which is characterized by the vertical flux convergence rate \( -\overline{\partial w \rho_C / \partial z} \). Consequently, we have

\[ \overline{\dot{w}} = 0 \]
\[ \mathbf{V} \cdot \overline{\mathbf{V}} = 0 \]
\[ M_C = 0 \]

and
\[ M_C + \overline{\mathbf{Q}_C} = \frac{\overline{\partial w \rho_C}}{\partial z}. \]
We expand the differential equations for $\zeta$, $\chi$, and $\delta_c$ given by (4) in a perturbation series and apply (7). The first-order terms and their solutions are as follows:

$$\frac{\partial \zeta}{\partial t} = w'$$
$$\frac{\partial \chi}{\partial t} = \nabla \cdot \mathbf{v}'$$
$$\frac{\partial \delta_c}{\partial t} = -\frac{Q_c}{\rho_c} + \frac{M_c + \bar{Q}_c}{\rho_c} \frac{\partial \rho_c}{\partial t}$$

where

$$\zeta = \int w'd\tau \approx -\frac{T'}{(\Gamma_{ad} + \bar{\epsilon}T'/\bar{\partial}z)} = -\frac{gT'}{N^2T}$$
$$\chi = \int \nabla \cdot \mathbf{v} \, d\tau \approx -\beta \frac{T'}{T}$$
$$\delta_c = -\int \left( \frac{Q_c}{[C]} - \alpha_m \frac{[C]}{[C]} \right) \, d\tau$$
$$|C| = \bar{\rho}_c$$
$$\alpha_m = (M_c + \bar{Q}_c)/|C|$$
$$\beta = \frac{(g/R - \Gamma_{ad})}{(\Gamma_{ad} + \bar{\epsilon}T'/\bar{\partial}z)} - 2.25 - 3.0.$$  

$\Gamma_{ad} = 9.5$ K/km is the adiabatic lapse rate, $T$ is temperature profile, $g = 9.5$ m$^2$/s is the gravitational acceleration, and $R = 287$ m$^2$K/s$^2$ is the gas constant for dry air. Notice that the first-order perturbation solution for $\delta_c$ is associated with the perturbed chemistry of the species and is related to $Q_c$ and $[C]$. The explicit solutions for $\zeta$ and $\chi$ for inert species as functions of the temperature perturbations shown in (9) are taken from Gardner and Liu [2010]. Because $\bar{Q}_c$ is small, $\alpha_m$ is approximately equal to the ratio of the meteoric influx to the species density. The inverse of this frequency represents the nominal time period required for the integrated meteoric input to equal the species density. For the mesospheric metals this time period is on the order of several days so that $\alpha_m$ is much smaller than the fluctuation frequencies.

The species and its chemical production and loss rates are perturbed by wave- and turbulence-induced temperature fluctuations ($T'$), vertical wind fluctuations ($\zeta$), wind divergence fluctuations ($\chi$), and chemical fluctuations ($\delta_c$). We assume that all of the species involved in the chemical production and loss processes, except $C$, are only weakly affected by chemical and so their perturbed densities are proportional to $e^{-\zeta}$. This is an approximation that is valid for ozone but not for the mesospheric metals, as we shall see in section 3 and Appendix A. Of course, the perturbed density of species $C$, which is only involved in the loss reactions, is proportional to $e^{-\chi}$. Thus, the perturbed production and loss terms are given by

$$P_c(T, z) = e^{-\zeta}P_{c1}(T, z - \zeta) + e^{-2\zeta}P_{c2}(T, z - \zeta) + e^{-3\zeta}P_{c3}(T, z - \zeta)$$
$$L_c(T, z) = e^{-\chi} \left[ e^{-\chi}L_{c1}(T, z - \chi) + e^{-2\chi}L_{c2}(T, z - \chi) + e^{-3\chi}L_{c3}(T, z - \chi) \right],$$

where the subscripts 1, 2, and 3 denote, respectively, the unimolecular, bimolecular, and termolecular reactions.

The perturbed parameters $[C]'$ and $Q_c'$ are derived from (9) and (10):

$$\alpha_m \frac{[C]'}{[C]} = -\alpha_m \left( \chi + \delta_c - \frac{\zeta}{\bar{\rho}_c} \right) \approx \alpha_m \frac{\partial \rho_c}{\partial t} + \frac{\alpha_m}{\bar{\rho}_c} \int w'd\tau + \alpha_m \int \left( \frac{Q_c}{[C]} - \alpha_m \frac{[C]}{[C]} \right) \, d\tau$$

$$H_c = -\left( \frac{1}{[C] \bar{\partial}z} \right)^{-1}$$

and
Because of the rate coefficients, which depend upon $T$, $a_c$ is a dimensionless scale factor that characterizes the sensitivity of the perturbed chemistry ($Q_c = \tilde{P}_c - \bar{L}_c$) to the temperature perturbations. It is related to the density fluctuations of all the species participating in the key reactions and to the temperature dependences of the reaction rates. $a_c$ can be either positive or negative depending on the species and its magnitude can be much larger than 1. By combining equations (11) and (12) and expressing $|C|$, $Q_c$, $T$, and $w$ in terms of their temporal Fourier transforms, we obtain

\[
\frac{Q_c}{|C|} = \frac{\alpha_c a_c}{|C|} \frac{T}{T} + \frac{1}{|C|} \frac{\partial Q_c}{\partial T} + \frac{1}{|C|} \frac{\partial Q_c}{\partial \chi} + \frac{1}{|C|} \frac{\partial Q_c}{\partial \delta_c} + \frac{1}{|C|} \frac{\partial Q_c}{\partial \zeta} \\
= a_c \left[ \frac{\alpha_c}{|C|} \frac{T}{T} + \frac{1}{|C|} \frac{\partial Q_c}{\partial T} \right]_{T=\text{const}} \int w'd\tau - a_c \left( \frac{Q_c}{|C|} - \alpha_m |C| \right) \right) d\tau
\]

(12)

For notational convenience in (12) we let $-\partial Q_c / \partial z |_{T=\text{const}} = \partial Q_c / \partial \zeta$ denote the derivative with respect to $z$ of only the species density profiles involved in the production and loss reactions. It does not include the derivatives of the rate coefficients, which depend upon $T$.

The effective vertical transport velocity of a constituent is defined as its vertical flux divided by its mean density. Because $\dot{Y}$, $w$, $\chi$, $\delta_c$, and $\zeta$ are all Gaussian distributed, the constituent transport velocity can be written as the sum of the dynamical (Dyn) and chemical (Chem) transport velocities (see (13) in Gardner and Liu [2010]):

\[
\bar{w}_c = \frac{w |C|}{|C|} = -\nabla \chi - \bar{w} \delta_c + \frac{\bar{w}_\zeta}{H_\zeta} = \bar{w}_c |\text{Dyn} | + \bar{w}_c |\text{Chem} |
\]

where

\[
\bar{w}_c |\text{Dyn} | = -\nabla \chi \pm \bar{w} \frac{T}{T} \\
\bar{w}_c |\text{Chem} | = -\bar{w} \delta_c = w \int \left( \frac{Q_c}{|C|} - \alpha_m |C| \right) d\tau
\]

and $\bar{w}_\zeta = w \int w' d\tau = 0$.

By combining (13) and (14), we obtain the following expression for the chemical transport velocity.

\[
\bar{w}_c |\text{Chem} | \geq S_T (a_c + \alpha_m) \left[ \frac{\alpha_c a_c - \alpha_m \beta}{N} \right] + \frac{g}{N^3} \left[ \frac{\partial Q_c}{\partial z} |_{T=\text{const}} + \frac{M_c |C|}{H_c} \right] \left[ \frac{g}{N} \left( \frac{T}{T} \right) \right] \\
+ S_{HF} (a_c + \alpha_m) \frac{(\alpha_c a_c - \alpha_m \beta) w_T}{(\alpha_c + \alpha_m)} \left. \frac{\partial Q_c}{\partial z} \right|_{T=\text{const}}
\]

where

\[
\alpha_c = \frac{L_c}{|C|}
\]

\[
\alpha_m = \frac{M_c + \bar{Q}_c |C|}{|C|} = \frac{1}{|C|} \frac{\partial w |C|}{\partial z}
\]

\[
S_T (a_c + \alpha_m) = \frac{1}{w_T} \frac{1}{2 \pi} \int_0^\pi \frac{\omega^2 F_{\omega}(\omega) d\omega}{\omega^2 + (\omega_c + \omega_m)^2}
\]

\[
S_{HF} (a_c + \alpha_m) = \frac{1}{w_T} \frac{1}{2 \pi} \int_0^\pi \frac{(\omega_c + \omega_m)^2 H_{\omega}(\omega) d\omega}{\omega^2 + (\omega_c + \omega_m)^2}
\]
For a single monochromatic wave or tide, the chemical transport is given by
\[ \text{Chemical transport} = \text{first term} + \text{second term} \]
where the first term is proportional to the temperature fluctuation variance, while the second is proportional to the heat flux. \( S_T(\omega_C + \omega_M) \) and \( S_{HF}(\omega_C + \omega_M) \) are dimensionless factors that represent the fractions of the total temperature variance and heat flux that contribute to the transport of \( C \). Both factors depend on \( \omega_C \) and \( \omega_M \). The derivation leading to (15) is general. We only assume that the wind fluctuations are small enough that the solutions to the differential equations for \( \zeta, \chi, \) and \( \delta_C \) can be accurately approximated by their first-order perturbation terms. Consequently, equation (15) is valid for fluctuations caused by both waves and turbulence. Note that for inert nonmeteoric species \( \omega_C = \omega_M = 0 \) and so the chemical flux is zero. For many nonmeteoric species, like ozone, the effective production or loss due to vertical fluctuations caused by both waves and turbulence is small compared to chemistry. Hence, we may assume the species is in chemical equilibrium and the chemical flux given by (15) reduces to the simple form:
\[ \mathcal{W}_C|_{\text{Chem}} = S_T(\omega_C) \frac{\omega_C}{\mathcal{N}} \frac{g}{\mathcal{N}} \frac{(T')^2}{T^2} + S_{HF}(\omega_C) \frac{\omega_C}{\mathcal{N}} \frac{W_T}{T} \]
when
\[ \mathcal{M}_C = 0 \]
and
\[ \mathcal{Q}_C = 0. \]

Chemical transport represents the net physical displacement of a species that results from the density fluctuations caused by its perturbed chemistry. If the species density is enhanced by the perturbed chemistry when the wave-induced vertical wind fluctuation is downward but depleted a half period later when the wind is upward, then there is a net downward transport of the species, and the chemical flux is negative. For a single monochromatic wave or tide, the chemical transport is given by
\[ \mathcal{W}_C|_{\text{Chem}} = \frac{\omega^2}{(\omega^2 + \omega_C^2)} \frac{\omega_C}{\mathcal{N}} \frac{g}{\mathcal{N}} \frac{(T'_W)^2}{2T^2} + \frac{\omega_C^2}{(\omega^2 + \omega_C^2)} \frac{\omega_C}{\mathcal{N}} \frac{HF_W}{T} \]
where
\[ T'_W = \text{wave temperature amplitude} \]
\[ HF_W = \text{wave heat flux} \]
\[ \omega = 2\pi/\tau = \text{wave frequency} \]
\[ \tau = \text{wave period}. \]

Notice that the wave frequency plays an important role. The highest frequency waves make a disproportionately large contribution to the chemical transport. Because the density fluctuations caused by low frequency waves \( (\omega < \omega_C) \) are chemically damped by the loss processes, the contributions of these waves to chemical transport are attenuated by the factor \( (\omega/\omega_C)^2 \), even though they may make a significant contribution to the temperature variance. Chemical damping is most significant if the chemistry is fast, i.e., if the loss rate and hence the cutoff frequency, are large.

Finally, it is important to note that vertical transport arises because of enhanced chemical production and/or loss associated with the wind and temperature fluctuations. Because the total amount of a chemically active species \( C_i \) in all the \( C \)-bearing compounds \( (\sum_i C_i) \) is conserved, there can be no chemical transport of the total constituent [see Gardner and Liu, 2010, paragraph 38]. In other words, the chemical transport of \( C \) must be balanced by the opposite transport of other \( C \)-bearing constituents. This result follows directly from the continuity equation for \( C_i \), because the chemical sources and sinks of all the \( C \)-bearing compounds must sum to zero.

**3. Wave-Induced Chemical Transport of Mesospheric \( O_3 \)**

The canonical power law spectrum of the temperature fluctuations induced by gravity waves is given by
\[
T^{\text{wave}}_{\text{f}}(\omega) = \begin{cases} 
\frac{2\pi(T_{\text{wave}})}{(1 - f/N)} & f \leq \omega \leq N \\
0 & \text{otherwise}
\end{cases}
\]

\(f = 2\pi/\tau_i = \text{inertial frequency}\)

\(N = \sqrt{\left(\Gamma_{\text{ad}} + cT/\partial z\right)g/T} = 2\pi/\tau_b = \text{buoyancy frequency}\)

\(\tau_i = \frac{12}{\sin|\phi|} = \text{inertial period}\)

\(\phi = \text{latitude}\)

\(\tau_b \approx 300 \text{ s = buoyancy period}\).

This form is based largely on observations, which show that the power law model provides a good fit to the high frequency range of the spectrum for periods ranging from about 12 h to the buoyancy period (~5 min). Observations also show that the spectral index is somewhat variable with a mean value of approximately –2 [e.g., see Gardner and Yang, 1998, Figure 5d]. Unfortunately, there have been no observations of, nor theoretical predictions for, the frequency distribution of the wave-induced heat flux. For an individual wave the heat flux is proportional to the product of the temperature and vertical wind amplitudes of the wave. For the idealized temperature spectrum given by (18), the temperature amplitude of a wave is proportional to \(\omega^{-1}\), and the vertical wind amplitude is proportional to \(\omega^0\), so in the absence of observations or other theoretical guidance, we assume that the heat flux distribution is proportional to \(\omega^{-1}\).

\[
H_{\text{wave}}(\omega) = \begin{cases} 
\frac{2\pi w_{\text{wave}} T_{\text{wave}}}{\ln(N/f)} & f \leq \omega \leq N \\
0 & \text{otherwise}
\end{cases}
\]

These idealized models must be modified for calculations at low latitudes less than 15–20° to account for the very small value of the inertial frequency, which is zero at the equator. At the lowest frequencies, the temperature spectrum and the heat flux distribution actually decrease with decreasing \(\omega\) since the magnitude must go to zero at \(f\). We use these models because they are applicable at the higher latitudes and higher frequencies corresponding to existing flux measurements, and they yield relatively simple expressions for the chemical transport. For many species, the chemical flux cutoff frequency is much larger than the inertial frequency but comparable to the buoyancy frequency so the behavior of the spectrum at low frequencies is not critical for calculating the chemical fluxes. The wave-induced chemical transport velocity for a nonmeteoric species like O₃ is calculated by substituting (18) and (19) into (15) with \(M_C = 0\).

\[
\begin{align*}
W_{\text{chem}}^{\text{wave}} &= S_{\text{wave}}^{\text{wave}}(\omega_C) \frac{\alpha_C}{N} \left(\alpha_C + g \frac{1}{N^2 \int_C \frac{\partial Q_C}{\partial z}} \right) \left(\frac{\left(T_{\text{wave}}\right)^2}{\tau^2} + S_{\text{HF}}^{\text{wave}}(\omega_C) \alpha_C \frac{w_{\text{wave}} T_{\text{wave}}}{T}\right) \\
\text{where} \quad Q_C &= \frac{\partial w_C}{\partial z} \\
S_{\text{wave}}^{\text{wave}}(\omega_C) &= \frac{f}{\omega_C} \tan^{-1}\left(\frac{N}{\omega_C}\right), \quad f = \omega_C \\
S_{\text{HF}}^{\text{wave}}(\omega_C) &= 1 + \frac{\ln\left(\frac{\omega_C}{\sqrt{N^2 + \omega_C^2}}\right)}{\ln(N/f)}, \quad f = \omega_C
\end{align*}
\]

\(\left(T_{\text{wave}}\right)^2\) and \(w_{\text{wave}} T_{\text{wave}}\) denote the total temperature variance and heat flux caused by all the waves in the spectrum.

Ozone chemistry plays key roles in the formation of mesospheric OH airglow and, as we will see in the next section, in the chemistry of the mesospheric metal layers. The important reactions for O₃ in the upper
atmosphere, above the stratopause, are described in detail by Allen et al. [1984], Walterscheid et al. [1987] and Smith et al. [2010]. The primary chemical source of O₃ is the reaction of O and O₂:

\[ \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \quad k_1 = 6.0 \times 10^{-34} \left( \frac{300}{T} \right)^{2.4}, \quad (21) \]

where \( \text{M} = \text{N}_2 + \text{O}_2 \). In the mesopause region below ~105 km, the chemical loss of O₃ is dominated by its reactions with H and O:

\[ \begin{align*}
\text{O}_3 + \text{H} & \rightarrow \text{O}_2 + \text{OH} \quad k_2 = 1.4 \times 10^{-10} \exp(-470/T) \\
\text{O}_2 + \text{O} & \rightarrow 2\text{O}_2 \quad k_3 = 8.0 \times 10^{-12} \exp(-2060/T).
\end{align*} \quad (22) \]

During the daytime, the photolysis of O₃ is also an important loss process:

\[ \begin{align*}
\text{O}_3 + h\nu & \rightarrow \text{O}_2 + \text{O} \quad k_4 = 8.0 \times 10^{-4} \\
\text{O}_3 + h\nu & \rightarrow \text{O}_2 + \text{O}(^{1}\text{D}) \quad k_5 = 5.1 \times 10^{-3} \quad J_{\text{O}_3} = 5.9 \times 10^{-3} \text{s}^{-1}. \quad (23)
\end{align*} \]

The rates for reactions (21) and (22) were obtained from Sander et al. [2006], while the photolysis rates for (23) were obtained from Allen et al. [1984]. Because the timescales for ozone production and loss are very short in the mesopause region above ~82 km, the assumption of photochemical equilibrium is valid [Smith et al., 2010] so that in the steady state production balances loss and

\[
\overline{Q}_{\text{O}_3} = \frac{\partial \omega_\text{O}_3}{\partial z} = k_1 [\text{O}][\text{O}_2][\text{M}] - (k_2 [\text{H}] + k_3 [\text{O}] + J_{\text{O}_3})[\text{O}_3] \\
[\text{O}_3] = \frac{k_1 [\text{O}][\text{O}_2][\text{M}] - \partial \omega_\text{O}_3/\partial z}{k_2 [\text{H}] + k_3 [\text{O}] + J_{\text{O}_3}} \cong \frac{k_1 [\text{O}][\text{O}_2][\text{M}]}{k_2 [\text{H}] + k_3 [\text{O}] + J_{\text{O}_3}},
\]

where \( J_{\text{O}_3} \) equals zero at night and 5.9 \times 10^3 \text{s}^{-1} during the day. Throughout the mesopause region the production or loss of O₃ associated with vertical flux convergence is less than ±1% of the production due to chemistry. Therefore, in deriving the steady state ozone density given by (24), the effects of vertical transport are neglected.

O and H have very long lifetimes in the mesopause region because they are only weakly dependent on chemistry [Walterscheid et al., 1987; Smith et al., 2010]. Therefore, we neglect the very small chemical perturbations of these species. The wave-induced chemical transport velocity of ozone is given by (20) with \( C = \text{O}_3 \) and \( \overline{Q}_{\text{O}_3} = 0 \):

\[
\overline{w}_{\text{O}_3}\text{Chem} = \frac{f}{N} \tan^{-1}(N/\omega_{\text{O}_3}) \omega_{\text{O}_3} \left( \frac{T_{\text{Wave}}}{T} \right)^2 \left[ 1 + \frac{\ln \left( \omega_{\text{O}_3}/\sqrt{N^2 + \omega_{\text{O}_3}^2} \right)}{\ln(N/f)} \right] \alpha_{\text{O}_3} \text{Wave} \frac{T_{\text{Wave}}}{T},
\]

where

\[
\omega_{\text{O}_3} = \frac{\overline{Q}_{\text{O}_3}}{[\text{O}_3]} \cong k_2 [\text{H}] + k_3 [\text{O}] + J_{\text{O}_3},
\]

\[
\alpha_{\text{O}_3} = 2\beta - 2.4 - k_3 [\text{H}] \left( 470K/T + \beta \right) - k_3 [\text{O}] \left( 2060K/T + \beta \right).
\]

Note that the constant 2.4 in the expression for \( \alpha_{\text{O}_3} \), is the contribution arising from the temperature dependence of \( k_1 \). The chemical transport velocity for O₃ is plotted in Figure 1a, and the chemical cutoff period is plotted in Figure 1b. These profiles were computed by using (25) and the profiles of \([\text{O}_3],[\text{O}],[\text{H}],\) and \( T \) that were measured by the Sounding of the Atmosphere using Broadband Emission Radiometry (SABER) instrument on the Thermosphere-Ionosphere-Mesosphere Energetics and Dynamics satellite. These values represent the zonal and annual means of 13 years of observations from January 2002 through December 2014 at the latitude of the Starfire Optical Range (SOR), NM (35°N). They were computed by averaging the SABER densities and temperatures over the 7 h periods centered at local midnight and local noon at SOR. The SABER \([\text{O}_3],[\text{O}],\) and \([\text{H}]\) profiles are plotted in Figure 2.
The temperature variance and heat flux profiles (annual mean) were obtained from the extensive nighttime lidar measurements made at SOR from June 1998 to November 2000 [see 

Gardner and Liu, 2007, 

Figure 2b or Figure 5b]. Because the mean observation period for the SOR data set was only 7.3 h, the measured wind and temperature data do not include waves with periods longer than about 10 h and so the magnitudes of the O

3 transport velocity profiles plotted in Figure 1a are somewhat smaller than expected for a full spectrum of waves. The uncertainties in the O

3 transport were assumed to be ±25% for the SOR temperature variance (takes into account the variable lidar observation periods), ±4% for the SABER temperatures, and ±50% for the SABER O and H densities, which were assumed to be uncorrelated. These values are conservative but realistic. To compute the daytime O

3 transport velocity and cutoff period, we assumed that the temperature variance was identical to the nighttime values. For comparison, the dynamical transport velocity measured at SOR, which is the same for all atmospheric constituents, is also plotted in Figure 1a [Gardner and Liu, 2010]. Note, we did not use the annual mean nighttime temperature profile measured by the lidar, which differs by at most ±4 K from the SABER profiles, because equation (24) was derived by assuming photochemical equilibrium. Thus, [O

3], [O], [H], and T must be obtained from the same source to ensure that (24) is valid. Furthermore, SABER provides observations during both night and day, while the lidar only measured the nighttime temperature and dynamical transport profiles.

The wave-driven chemical transport of O

3 is small below 90 km during both day and night. Above 90 km it is downward at night with values increasing from about 0 at 90 km to ~2.5 cm/s at 100 km. However, during the day the chemical transport is upward above 90 km with values peaking at about +0.75 cm/s near 94 km. The significant differences between the downward nighttime and upward daytime transport, especially at the higher altitudes, are a direct result of the large diurnal variations in the O

3 loss processes, which are dominated by H at night and by photolysis during the day. During the night the chemical cutoff period (\(\tau_{O_3}\)) varies from about 40 min near 85 km to more than 200 min near 100 km so that waves with periods ranging from the buoyancy period up to several hours contribute to nighttime chemical transport. At this latitude the cutoff frequency that maximizes chemical transport is about 80 min, which occurs for O

3 near 95 km during the night where the H density is \(\sim 10^8\) cm\(^{-3}\). However, during the day photolysis increases the loss of O

3 and decreases the cutoff period to 12–15 min. Only the shortest period waves, near the buoyancy period,
contribute to the daytime chemical transport of $O_3$. However, daytime photolysis also changes the sign of $\alpha_{O_3}$. The combined effects of the strong diurnal variations in both $\tau_{O_3}$ and $\alpha_{O_3}$ result in substantially different profiles for the nighttime and daytime chemical transport velocities. Even though the $O_3$ chemical transport changes substantially between day and night, the impact on the $O_3$ density is small because the associated vertical flux convergence is small compared to chemical production and loss. However, as we shall see in the next section, vertical transport has a significant impact on the densities of the meteoric metal layers.

4. Wave-Induced Chemical Transport of the Mesospheric Na and Fe

During the past several decades numerous researchers, using a combination of atmospheric observations, laboratory measurements of key reaction rates, and atmospheric modeling, have studied the chemistries of the mesospheric metal layers in considerable detail [e.g., McNeil et al., 2002; Plane, 2003; Plane et al., 2015]. The layers form by the injection of atoms into the lower thermosphere and upper mesosphere, between ~70 and ~120 km altitude, through the vaporization of high-speed cosmic dust particles. The sputtered and ablated atoms, some of which are ionized by hyperthermal collisions with air molecules, are then transported downward by advection, eddy diffusion, and wave effects to chemical sinks below about 85 km. Ion chemistry predominates above about 100 km and neutral chemistry below.

The chemistry of the metals is far more complicated than the chemistry of ozone. Note, in this section and in Appendix A, we adopt the reaction numbering scheme used by the University of Leeds group to characterize the gas-phase chemistries of mesospheric Na and Fe. Above 85 km the chemical losses of Na and Fe are controlled by a series of reactions, which are listed in Tables 1 and 3 of Plane et al. [2015] along with the reaction rates. Several of the reaction rates have been updated recently, and they are summarized in Tables 1 and 2 of this paper. Between about 85 and 100 km, the chemical losses of the metals, due to their reactions with $O_3$, are significantly larger than the losses from all of the other processes combined. However, this reaction produces the metal oxide, which reacts with $O$, to quickly recycle the metals back to their atomic forms. Because of this recycling, both Na and Fe behave much like inert species between 85 and 100 km, where the meteoric influx is balanced by downward transport to maintain the steady state layer profiles. Below 90 km, where the $O$ density decreases rapidly with decreasing altitude, while the densities of $O_2$, $CO_2$, $H_2O$, and $H_2$ increase, this recycling is inhibited as the metals are tied up in more stable reservoirs such as NaOH, NaHCO$_3$, FeO$_3$, Fe(OH)$_2$, and FeOH [Plane et al., 2015]. Above about 95 km, reactions of both metals with $O_2^+$ and NO$^+$ create metals ions, which is a stable reservoir for Fe but not for Na below 95 km (see Appendix A for details). Of course, during the day, photoionization is an additional loss process for both species. Even though the loss rates are

Table 1. Updated Na Reaction Rates

<table>
<thead>
<tr>
<th>Number</th>
<th>Reaction</th>
<th>Rate</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>R4</td>
<td>$NaO + H_2 \rightarrow NaOH + H$</td>
<td>$k_4 = 4.9 \times 10^{-1}^{\text{a}}$</td>
<td>Gómez Martín et al. [2015]</td>
</tr>
<tr>
<td>R5</td>
<td>$NaO + H_2 \rightarrow Na + H_2O$</td>
<td>$k_5 = k_4$</td>
<td>Gómez Martín et al. [2015]</td>
</tr>
<tr>
<td>R6</td>
<td>$NaO + H_2O \rightarrow NaOH + OH$</td>
<td>$k_6 = 5.06 \times 10^{-10}^{\text{b}} \exp(-240/T)$</td>
<td>Gómez Martín et al. [2015]</td>
</tr>
<tr>
<td>R7</td>
<td>$NaOH + H \rightarrow Na + H_2O$</td>
<td>$k_7 = 3.9 \times 10^{-11}^{\text{c}}$</td>
<td>J. C. Gómez Martín, personal communications, 2015</td>
</tr>
<tr>
<td>R8</td>
<td>$NaOH + CO_2 + M \rightarrow NaHCO_3$</td>
<td>$k_8 = 2.3 \times 10^{-28}^{\text{d}}(T/300)^{4.12}$</td>
<td>Gómez Martín et al. [2015]</td>
</tr>
<tr>
<td>Rx</td>
<td>$NaO + O_3 \rightarrow NaO_2 + O_2$</td>
<td>$k_x = 1.1 \times 10^{-3}^{\text{e}} \exp(-568/T)$</td>
<td>J. M. C. Plane, personal communications, 2015</td>
</tr>
</tbody>
</table>

Figure 2. SABER $O_3$, $O$, and $H$ densities plotted versus altitude.
small, Na and Fe are slowly depleted between 85 and 100 km as both species are converted, at least temporarily, to Na\(^+\), NaOH, NaHCO\(_3\), Fe\(^{+}\), FeO\(_2\), Fe(OH)\(_2\), and FeOH. These loss processes contribute to chemical transport.

Because of the multiplicity of reactions and their speeds, the computation of the chemical transport velocities for Na and Fe is far more involved than that for O\(_3\). The details are outlined in Appendix A, and the final results are given by equation (A8) for Na and (A16) for Fe. While complex, the various terms in these formulas are identical in form to that given by equation (15). For Na the \(V_{\text{Na}}\) \((\alpha_{\text{Na}}\omega)\) and \(V_{\text{NaOH}}(\alpha_{\text{NaOH}}\omega)\) terms represent the contributions to chemical transport associated with the Na that is temporarily stored as Na\(^+\) and NaOH and is then recycled back to atomic Na. The magnitudes of these contributions depend on the Na\(^+\) and NaOH densities and on the recycling speeds, which are dependent on \(\omega_{\text{Na}}\) and \(\omega_{\text{NaOH}}\). The \(V_{\text{NaOH}(0)}\) term represents an additional contribution associated with the NaOH that is converted to the stable reservoir NaHCO\(_3\). The \(V_{\text{Na}}\) term is only significant during the day when the NO\(^+\) and O\(_2\)^\(^+\) densities are large, and Na is photoionized. The \(V_{\text{NaOH}}\) terms are only significant below 85 km where the density ratio [NaOH]/[Na] becomes sufficiently large. The \(V_{\text{Na}(0)}\) term represents the contributions to chemical transport associated with the meteoric influx \((M_{\text{Na}} > 0)\) and net loss of Na \((\overline{Q}_{\text{Na}} = -L_{\text{Na}}^{\text{Net}} < 0)\), which results in its departure from chemical equilibrium. In fact, during the nighttime between 85 and 100 km, this term dominates the chemical transport of Na.

\[
\overline{M}_{\text{Na}} \equiv V_{\text{Na}}(0) \equiv \frac{g}{N^1} \left( \frac{\partial}{\partial z} \left( \frac{\overline{M}_{\text{Na}}}{{|Na|}} \frac{1}{z} \frac{\partial |Na|}{\partial z} \right) \right) \frac{g(T)}{T^3}
\]

85 km < z < 100 km at night

where

\[
\overline{Q}_{\text{Na}} = -L_{\text{Na}}^{\text{Net}} = -k_{\text{Na}}[\text{CO}_2][\text{M}][\text{NaOH}]
\]

\[
\overline{\omega}_{\text{Na}} = \frac{L_{\text{Na}}^{\text{Net}}}{[\text{Na}]} = \frac{k_{\text{Na}}[\text{CO}_2][\text{M}][\text{NaOH}]}{[\text{Na}]}
\]

According to the continuity equation, for Na the meteoric influx plus the total Na vertical flux convergence should equal the net chemical production/loss rate (see equation (7)):

\[
M_{\text{Na}} - \frac{\partial \overline{M}_{\text{Na}}}{\partial z} = L_{\text{Na}}^{\text{Net}} = k_{\text{Na}}[\text{CO}_2][\text{M}][\text{NaOH}]
\]

or

\[
\overline{w'}[\text{Na}] = -\int \overline{M}_{\text{Na}}dz + \int L_{\text{Na}}^{\text{Net}}dz.
\]

Therefore, the total Na flux is equal to the difference between integrated meteoric influx and chemical losses from above. In the absence of chemical loss (or horizontal transport), the Na flux is negative, and its magnitude increases monotonically with decreasing altitude, reaching a maximum value equal to the total integrated meteoric influx. Below 90 km chemical losses become important, and the flux begins to decrease as the integrated chemical loss rate increases. At the bottom of the Na layer near 80 km where the Na density is zero, the Na flux is also zero, and the total meteoric influx is balanced by the total chemical loss. Above the peak of the flux profile, the flux convergence is negative which means atomic Na is being transported out of this region. Below the peak the flux convergence is positive, as Na is transported into this region. Measurements of the Na flux profiles at several sites with Doppler lidars exhibit these general characteristics with the maximum downward Na flux occurring near 86–88 km [e.g., Gardner and Liu, 2010; Huang et al., 2014].
To test this relationship between vertical flux convergence and chemical loss quantitatively, we use the extensive nighttime measurements of gravity wave perturbations of winds, temperatures, and Na densities made in 1998–2000 at the Starfire Optical Range (35°N, 106.5°W), NM using a Na Doppler lidar. All of the wave-induced vertical fluxes were derived from this data set [Gardner and Liu, 2007, 2010]. In particular, the vertical flux convergence associated with dynamical and chemical transport of Na was computed (see Figure 4a and Table 3) [Gardner and Liu, 2010]. We added to those values, the eddy flux convergence, calculated by assuming $k_{zz} = 50 \text{ m}^2/\text{s}$ at all altitudes between 85 and 100 km, to get the total Na flux convergence. Finally, we added the $M_{Na}$ values calculated for the Zodical Cloud Particle Model [Nesvorny et al., 2010, 2011] using the Chemical Ablation Model (CABMOD) developed at the University of Leeds [Vondrak et al., 2008; Carrillo-Sánchez et al., 2015].

These data sets were smoothed in two ways. First, the measured flux convergence at 90 km, which is an outlier, was replaced by the value predicted by a linear fit to all of the measurements between 85 and 100 km. Second, the CABMOD data were smoothed by fitting a quadratic polynomial to the values between 85 and 100 km and then scaled to correspond to a global Na vapor influx of 337 kg/d. The net chemical loss rate given by (26) was calculated using the [H$_2$O] and [H$_2$] profiles predicted by WACCM and the [O$_3$], [O], and [H] profiles measured by SABER, and the CO$_2$ profile is taken from Beagley et al. [2010]. The results are plotted in Figure 4. The uncertainties in the theoretical values for the chemical loss are dominated by the uncertainties in the densities of these species. The agreement between the measured and theoretical loss rates is excellent. The correlation between these two profiles exceeds 0.98.

The nighttime and daytime chemical transport profiles for Na predicted by (A8) are plotted in Figure 5. For comparison the measured nighttime dynamical and chemical transport velocity profiles measured at SOR are also included. These profiles are the annual mean values. The theoretical value for the Na chemical transport was calculated using the [O$_3$], [O], and [H] profiles measured by SABER, which are plotted in Figure 2, the [H$_2$O] and [H$_2$] profiles predicted by WACCM (Figure 3), the [O$_2$$^+$] and [NO$^+$] profiles from the IRI-2012 Reference Model (Figure 3), and the CO$_2$ profile is taken from Beagley et al. [2010]. Ozone has a strong diurnal variation with maxima near 4 LT and 19 LT and minima near 0 LT and 10 LT [Smith et al., 2013]. The SABER means were computed by averaging the O$_3$, O, and H densities over the 7 h periods centered at local midnight and local noon at SOR. The uncertainties in the predicted transport velocities were computed by expressing the [O$_3$] uncertainties in terms of the SABER [O] and [H] uncertainties using equation (24) and by assuming that the uncertainty in [M] is negligible. We also assumed a conservative ±50% for the density uncertainties of the remaining species. The predicted chemical transport is primarily upward during both day
and night. The velocities are generally small with the largest values of 1.7 cm/s at 85 km at night and 0.35 cm/s at 95 km during the day. The relatively large value at 85 km at night arises from the vertical gradient of \( \frac{\partial [\text{Na}]}{\partial z} \), measured at the Starfire Optical Range, New Mexico (35°N, 106.5°W) (blue curve), with the theoretical net chemical loss rate \( L_{\text{Na}}^{\text{loss}} = k_1 [\text{CO}_2] [\text{M}] [\text{NaOH}] \) (red curve).

Figure 4. Comparison of the net Na loss rate associated with the meteoric influx and vertical flux convergence \( M_{\text{Na}} + \frac{\partial}{\partial t} [\text{Na}] \) measured at the Starfire Optical Range, New Mexico (35°N, 106.5°W) (blue curve), with the theoretical net chemical loss rate \( L_{\text{Na}}^{\text{loss}} = k_1 [\text{CO}_2] [\text{M}] [\text{NaOH}] \) (red curve).

...fluxes for O, H, O\(_2\), CO\(_2\), O\(_2^+\), and NO\(^+\), which are required to compute the theoretical transport, may not represent the conditions in the mesopause region at SOR when the flux measurements were made in 1998–2000. For example, the theoretical transport depends on both the magnitudes and vertical gradients of these species, while the loss rate depends only on their magnitudes. Similarly, the measured flux convergence depends on both the magnitudes and vertical gradients of the vertical transport velocity and Na density, while the flux depends only on their magnitudes.

A potential source of bias in the measured chemical transport velocity is correlation between the measured vertical wind and vertical displacement fluctuations given in (14) by the term:

\[
\frac{\langle w_z \rangle}{H_{\text{Na}}} = - \frac{1}{[\text{Na}]} \frac{\partial [\text{Na}]}{\partial z} \left[ w \int w \, dr \right]_{\Delta t} = - \frac{1}{[\text{Na}]} \frac{\partial [\text{Na}]}{\partial t} \int_{\Delta t/2}^{\Delta t} \left[ w \int w \, dr \right] \, dt
\]

which is assumed to be zero. Statistically, this is a valid assumption, but in practice, the ensemble average is approximated by a time (sample) average. Hence, the time average will be small or zero only if the data are averaged over many or an integral number of wave periods. The mean observation period for the SOR measurements was about 7.3 h centered at local midnight [Gardner and Liu, 2007]. To remove the effects of the long period waves and tides, the perturbation quantities (and fluxes) were computed by subtracting a linear trend in time from the wind, temperature, and density profiles. Then numerous nights of flux measurements were averaged to produce the transport profiles plotted in Figure 5. Even so, it is possible that the residual effects of strong tides and long period waves could still contribute a bias in the flux and transport velocity measurements. We expect the nightly biases associated with waves to average incoherently to a small mean value, because of the wave phases and periods vary randomly from night to night. However, the tidal phases are quite stable in the mesopause region, and the observations were conducted primarily during the \( \sim 7.3 \) h periods centered at local midnight, so the nightly biases associated with tides are expected to average coherently. Thus, if this term is the source of the apparent bias in the measured Na chemical transport, it is most likely associated with atmospheric tides. Notice that the bias term is proportional to the gradient of the Na...
layer profile, which is large on the layer top and bottom sides and zero at the peak near 91 km. In fact, the measured Na chemical transport is minimum at the peak of the annual mean Na layer, where this bias term should be small. Additional observations, especially during the daytime and over longer observation periods, would help resolve the discrepancies between the theory and measurements and in particular, would provide insight on the apparent weak diurnal variations of the Na chemical transport that is predicted by the theory.

Because their chemistries are quite different, we expect the chemical transport of Fe to differ from that for Na. The predicted Fe chemical transport given by equation (A16) is plotted in Figure 6 for both day and night. For these calculations the Fe layer was modeled as a Gaussian distribution with a centroid height of 88 km and root-mean-square (RMS) width of 3.5 km which is consistent with midlatitude measurements in the Northern Hemisphere. Like Na, the Fe chemical transport between 85 and 100 km is dominated by the \( V_{Fe}(0) \) term.

\[
\overline{V}_{\text{Fe,chem}} \approx V_{Fe}(0) \approx - \frac{g}{N^2} \left( \frac{\partial \sigma_{Fe}}{\partial z} + \frac{M_{Fe}}{[Fe]} \frac{1}{N} \frac{\partial [Fe]}{\partial z} \right) \frac{g}{T} \left( \frac{T}{T_0} \right)^2
\]

85 km < z < 100 km

where

\[
\overline{Q}_{Fe}^\text{Net} = - \left( k_{13} [FeOH]^2 + k_{18} [NO^+] [Fe] + k_{19} [O_2^+] [Fe] + J_{33} [Fe] \right)
\]

\[
\sigma_{Fe} = \frac{k_{13} [FeOH]^2}{[Fe]} + k_{18} [NO^+] + k_{19} [O_2^+] + J_{33}
\]

During the night below 90 km the net Fe loss, due to dimerization of FeOH, and \( \sigma_{Fe} \) both increase rapidly with decreasing altitude so that the resulting Fe chemical transport is upward and also increases rapidly with decreasing altitude. The dynamical flux, which is proportional to heat flux, and the associated dynamical vertical flux convergence both go to zero at the lower altitudes. Therefore, the positive vertical flux convergence, associated with Fe chemical transport, is required to balance the increasing chemical loss of Fe at the lower altitudes.

During the day, the Fe chemical transport below 90 km is much smaller than at night, because FeOH is photolyzed to produce Fe and so the permanent loss of Fe decreases. This behavior helps explain the strong diurnal variations of Fe that have been observed on the layer bottomside [Yu et al., 2012]. The Fe density is enhanced below 85 km during the day because of photolysis, and this recycled Fe remains in this region because the vertical transport is weak.

Figure 5. Wave-induced dynamical and chemical transport velocities of Na plotted versus altitude. The measured profiles are the annual mean values observed with a Na Doppler lidar at the Starfire Optical Range, NM (35°N, 106.5°W). The predicted chemical transport was calculated using equation (A8) and the constituent profiles for the latitude of SOR derived from SABER measurements (Figure 2), WACCM (Figure 3a) and IRI-2012 (Figure 3b, see text for details).
The strong upward transport near 100 km and its diurnal variation are associated with the losses resulting from the production of Fe\(^{+}\), which is stronger during the day, and the large Fe density gradient at this high altitude which is more than 10 km above the layer peak. Near 100 km, the vertical gradient of \(\omega_{\text{Fe}}\) is positive, so the contribution of this term to chemical transport is downward, and it is much stronger during the day. However, the Fe density gradient is negative and quite large near 100 km, so that the term related to \(M_{\text{Fe}}\) dominates and makes a large positive contribution to the Fe chemical transport. Consequently, the net transport is strongly upward during the night and somewhat weaker during the day. In particular, the predicted upward chemical transport of Fe near 100 km is much stronger than the upward chemical transport of Na. This may partially explain why the tenuous Fe layers that have been observed in the lower thermosphere up to 170 km are more common and have higher densities than the thermospheric Na layers.

The differences between the Na and Fe chemical transport velocities below 90 km are significant. While both are upward, the Fe transport is much stronger. A limited set of Na and Fe vertical flux observations were made at night in August and September 2010 at the Table Mountain Lidar Facility just north of Boulder, CO [Huang et al., 2014]. The wave-induced vertical transport velocity profiles derived from these observations are plotted in Figure 7. These measurements were made simultaneously by probing a common volume of the atmosphere with Na and Fe lidars. Since the dynamical transport is identical for both species, the differences in these velocity profiles are due entirely to differences in their chemical transport. The measurements are qualitatively consistent with our theoretical predictions. Because the Na chemical transport is weakly upward below 90 km, while the Fe chemical transport is strongly upward during the night, the measured Na dynamical plus chemical transport velocity is much more negative than for Fe below 90 km. Above 95 km where the dynamical transport of both species is negligible, the measured Na and Fe transport velocities are both small, as expected.

Finally, it is important to note that below 90 km, the chemical transport of both Na and Fe is largely controlled by...
O$_3$ because the reaction of these metals with O$_3$ are the first steps leading to the formation of the stable reservoirs NaHCO$_3$ and FeOH. Above 95 km, the chemical transport of Na is weak, while the upward transport of Fe is controlled by NO$^+$ and O$_3^+$, which react with Fe to form the stable reservoir Fe$^+$.

5. Turbulence-Induced Chemical Transport of O$_3$ and the Mesospheric Metals

The turbulence-induced (eddy) chemical transport for O$_3$ is given by (16):

\[ W_{O_3}^{\text{Turb}} = S_T^{\text{Turb}}(\alpha_{O_3}) \frac{\alpha_{O_3}}{N} g \frac{(T_{\text{Turb}})^2}{\tau} + S_{HF}^{\text{Turb}}(\alpha_{O_3}) \frac{W_{\text{Turb}} T_{\text{Turb}}}{\tau} \]

where

\[ S_T^{\text{Turb}}(\alpha_{O_3}) = \frac{1}{(T_{\text{Turb}})^2} \int_0^\infty \frac{\omega^2 F_{\text{Turb}}(\omega)}{\omega^2 + \omega_o^2} d\omega \]

\[ S_{HF}^{\text{Turb}}(\alpha_{O_3}) = \frac{1}{W_{\text{Turb}} T_{\text{Turb}}} \int_0^\infty \frac{\omega^2 F_{\text{HF}}(\omega)}{\omega^2 + \omega_o^2} d\omega \]

To evaluate (30), we need to know the temporal spectrum of the temperature fluctuations and the frequency distribution of the eddy heat flux. Normally, the spectrum is modeled by assuming that the turbulence vortices are advected horizontally by the winds to generate the temporal fluctuations [Taylor, 1938]. This yields the familiar $\omega^{-5/3}$ power law shape for the frequency spectrum of the temperature fluctuations. However, the expression for the chemical flux was derived by solving the continuity equation in the reference frame that is moving with mean wind field (see equation (3)). Therefore, we need to know the intrinsic frequency distributions of the temperature variance and heat flux, caused by the chaotic vertical motions of the turbulent vortices. These are the distributions that would be observed when the mean wind field is zero. Unfortunately, theoretical and observational insights into the shape and frequency range of the intrinsic temperature spectrum are limited, and there are no theoretical models for, nor measurements of, the frequency distribution of the eddy heat flux.

It is well known that the spatial spectrum of vertical winds varies as $k^{-5/3}$ [e.g., Lumley, 1964]. If we assume that the intrinsic wind spectrum varies as $\omega^{-5/3}$, then the intrinsic temperature spectrum varies as $\omega^{-11/3}$, and the low-frequency cutoff of the turbulence fluctuations is (see Appendix B) as follows:

\[ \omega_o = 2\pi / \tau_o = N / \sqrt{8}. \] (31)

The corresponding cutoff period is about 14 min at mesopause heights. With this model the temperature and vertical wind amplitudes vary as $\omega^{-11/6}$ and $\omega^{-5/6}$, respectively, and so we assume that the eddy heat flux magnitude varies as $\omega^{-8/3}$. $S_T^{\text{Turb}}$ and $S_{HF}^{\text{Turb}}$ can be evaluated numerically by integrating over the assumed models for the intrinsic turbulence spectrum and heat flux distribution. $S_T^{\text{Turb}}(\alpha_{O_3}) = 1$ at night but is less than 1 during the day because the O$_3$ cutoff period is comparable to or smaller than $\tau_o$. On the other hand, $S_{HF}^{\text{Turb}}(\alpha_{O_3})$ is small (<1) for O$_3$ during both day and night. Because the effective cutoff frequencies are so small, the eddy chemical transport velocities for Na and Fe are simply given by (A8) and (A16) with $\tau_o$ replaced by $l_0$.

For turbulence, the variance of the relative temperature fluctuations can be expressed in terms of the energy dissipation rate $\varepsilon$, the outer scale of turbulence $l_o$, and the eddy diffusivity $k_{zz}$ (see equation (11) in Lübken [1997]) with $l_{\text{Max}}$ replaced by $l_o$:

\[ \frac{\text{Var}(T_{\text{Turb}})}{\tau^2} = 0.8703 \left( \frac{N}{g} \right)^2 \left( \omega_o \right)^{2/3} \approx \frac{2N^2}{g^2} W_{\text{Turb}} = \frac{5N^3}{g^2} k_{zz}. \] (32)

where we have used the following relationships derived by Weinstock [1978, 1981] to obtain the right-hand side of (32).
\[ k_{zz} = 0.81 \frac{E_N}{N^2} \]
\[ w_{\text{Turb}}^2 = \frac{\varepsilon}{0.49N^2} \geq 5 N k_{zz} \]
\[ \kappa_0 = \frac{2\pi}{l_0} \geq 0.9 - \frac{N}{w_{\text{Turb}}} \]
\[ l_0 \approx 9.973 \varepsilon^{1/2} N^{-1/2} \geq 11 \sqrt{\frac{k_{zz}}{N}} \]

\[ w_{\text{Turb}}' T_{\text{Turb}}' T \geq \frac{w_{\text{Turb}}' T_{\text{Turb}}' \theta}{C_0} \]

\( w_{\text{Turb}}' T_{\text{Turb}}' \theta = \frac{N^2}{g} k_{zz} \).

\[ \frac{w_{\text{Turb}}' T_{\text{Turb}}' \theta}{T} \geq \frac{w_{\text{Turb}}' T_{\text{Turb}}' \theta}{\frac{g}{T} \frac{k_{zz}}{g}} \]

where \( \theta \) is the potential temperature. If \( k_{zz} = 50 \text{ m}^2/\text{s} \), \( \tau_B = 5 \text{ min} \), and \( T = 200 \text{ K} \), 32–34 yield values of 1.6 m/s for the (RMS) vertical wind fluctuations and 1 K for the (RMS) temperature fluctuations and \(-0.23 \text{ cm/s} \) for the eddy heat transport velocity. For comparison, the measured (RMS) temperature fluctuations caused by gravity waves are about 8.4 K, while the gravity wave vertical wind fluctuations are about 2 m/s, and the gravity wave heat transport is \(-1.4 \text{ m/s} \) [Gardner and Liu, 2007]. For \( O_3 \), even though the wave-induced temperature variances are 70 times larger than for turbulence, the effects of the long-period waves are significantly damped by chemistry, while the high-frequency turbulence fluctuations are not. Consequently, the resulting wave- and turbulence-induced chemical transport velocities for \( O_3 \) are comparable. The eddy chemical transport velocities for Na and Fe, which are proportional to the temperature variance, are approximately 70 times smaller than the wave-induced values plotted in Figures 5 and 6 and so they are negligible.

For \( O_3 \) the eddy chemical transport is obtained by substituting (32) and (34) into (30).

\[ W_{O_3}^{\text{Turb}} = \left( \frac{1}{H_P} - \frac{1}{H_T} - \frac{1}{H_C} \right) k_{zz} \]

The expression for eddy dynamical transport associated with turbulent mixing is as follows:

\[ W_{\text{C|eddy}} = \left( \frac{1}{H_P} - \frac{1}{H_T} - \frac{1}{H_C} \right) k_{zz} \]

where

\[ H_P = \frac{R T}{g} \] pressure scale height

\[ H_T = \left[ -\frac{1}{T C_\theta} \right]^{-1} \] mean temperature scale height.

Notice that both are proportional to \( k_{zz} \), but the chemical transport is clearly nondiffusive because it is independent of the species concentration gradient.

The eddy diffusivity is difficult to measure in the mesopause region, and so there have been few observations of this important parameter. The most reliable data have been acquired using rocket-borne ionization gauge measurements of neutral density fluctuations, but the data are sparse. For this reason, we evaluated (35) and (36) by using a fixed value for \( k_{zz} \) of 50 m²/s at all altitudes, which is the annual mean value at SOR near 90 km [Gardner et al., 2014]. The eddy chemical and dynamical transport profiles for \( O_3 \) are plotted in Figure 8.
During the night, the chemical transport of O\textsubscript{3} is downward, but it is negligible compared to the eddy dynamical transport. During the day it is upward reaching values of about +0.5 cm/s between 90 and 95 km. Although the eddy dynamical transport of Na and Fe is important, the eddy chemical transport is negligible.

6. Discussion and Conclusions

The chemical flux of a species represents real physical transport. It arises because the density fluctuations of a species, caused by wave- and turbulence-induced perturbations of its chemistry, are strongly correlated with the vertical wind fluctuations. Chemical transport depends on the timescale of the wave and turbulence fluctuations. If the timescale is sufficiently long, then chemical reactions will damp the species density fluctuations, and the chemical transport will be small. Consequently, it is the short-period waves and turbulence that make the most significant contributions to chemical transport.

Although we used O\textsubscript{3} and the mesospheric metals to illustrate the characteristics of chemical transport, the theoretical derivations are general and can be applied to any neutral, chemically active atmospheric constituent. Chemical transport is proportional to the wave- and turbulence-induced temperature variances and heat fluxes and is nondiffusive in character. However, the chemical transport associated with turbulence can be expressed in terms of the eddy diffusivity (equation (35)), so that it can be included in atmospheric models by simply adding it to the eddy dynamical transport term. In fact, because turbulence is generated by breaking waves, \( k_{zz} \) and the wave-induced temperature variance and heat flux are all directly related to the intensity of the wave activity. Large-amplitude waves induce stronger temperature fluctuations and are also more prone to breaking, which generates more turbulence and increases \( k_{zz} \) and the heat flux [e.g., Zhao et al., 2003]. Therefore, \( k_{zz} \) could be used in atmospheric models as a proxy for both the temperature variance and heat flux. \( \text{Var}(T_{\text{Wave}}) \) is about 70 times larger than \( \text{Var}(T_{\text{Turb}}) \) at 87.5 km at SOR, while the wave-induced heat flux is about 6.5 times larger than the eddy heat flux. Hence, for modeling purposes we can use the following proxies for the temperature variance and heat flux:

\[
\frac{g}{N} \left( \frac{T_{\text{Wave}}}{\tau} \right)^2 - 70 \frac{g}{N} \left( \frac{T_{\text{Turb}}}{\tau} \right)^2 \cong \frac{350N^2}{g} k_{zz} \quad (37)
\]

\[
\frac{W_{\text{Wave}} T_{\text{Wave}}}{\tau} = 6.5 \frac{W_{\text{Turb}} T_{\text{Turb}}}{\tau} \cong \frac{6.5N^2}{g} k_{zz}.
\]

In this way, both the wave- and turbulence-induced chemical transport could be modeled by combining them with the eddy dynamical transport and using a common value of \( k_{zz} \) to represent these three transport processes. This approach also eliminates the inherent deficiencies of the idealized power law model for the low-frequency behavior of the gravity wave temperature spectrum, especially at low latitudes. Because chemical damping greatly attenuates the effects of all waves with frequencies less than the cutoff frequency, the latitudinal variation of the chemical flux is more realistically proportional to \( k_{zz} \) rather than \( f \left( \frac{T_{\text{Wave}}}{\tau} \right)^2 \), which is clearly not valid at the equator where \( f = 0 \). For example, the WACCM wave parameterization scheme shows that the zonal and annual mean \( k_{zz} \) at 87.5 km is small near the equator with values \( \sim 15 \text{ m}^2/\text{s} \), and it peaks in both hemispheres at high latitudes near 60° with values \( \sim 80 \text{ m}^2/\text{s} \) [see Gardner et al., 2014, Figure 1b].

Chemical transport of O\textsubscript{3} is controlled by H and O, while the transport of Na and Fe are controlled by O\textsubscript{3}, O, H\textsubscript{2}O, H\textsubscript{2}, O\textsubscript{2}+, and NO\textsuperscript{+}. These species determine the cutoff frequencies, and hence the magnitudes of the transport velocities. Because the densities of H, O, O\textsubscript{3}, O\textsubscript{2}+, and NO\textsuperscript{+} exhibit strong diurnal variations, while photolysis and photon-ionization during the day also impact transport, the chemical transport of O\textsubscript{3}, Na, and Fe are different between night and day.

The theoretical formulas were qualitatively validated by comparing predictions with nighttime measurements of the wave-induced chemical fluxes of Na and Fe. Lidar measurements of both the wave- and turbulence-induced fluxes of other species would be especially useful in helping to further validate and refine them with the eddy dynamical transport and using a common value of \( k_{zz} \) to represent these three transport processes. This approach also eliminates the inherent deficiencies of the idealized power law model for the low-frequency behavior of the gravity wave temperature spectrum, especially at low latitudes. Because chemical damping greatly attenuates the effects of all waves with frequencies less than the cutoff frequency, the latitudinal variation of the chemical flux is more realistically proportional to \( k_{zz} \) rather than \( f \left( \frac{T_{\text{Wave}}}{\tau} \right)^2 \), which is clearly not valid at the equator where \( f = 0 \). For example, the WACCM wave parameterization scheme shows that the zonal and annual mean \( k_{zz} \) at 87.5 km is small near the equator with values \( \sim 15 \text{ m}^2/\text{s} \), and it peaks in both hemispheres at high latitudes near 60° with values \( \sim 80 \text{ m}^2/\text{s} \) [see Gardner et al., 2014, Figure 1b].

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The theoretical formulas were qualitatively validated by comparing predictions with nighttime measurements of the wave-induced chemical fluxes of Na and Fe. Lidar measurements of both the wave- and turbulence-induced fluxes of other species would be especially useful in helping to further validate and refine
the theoretical predictions. In particular, daytime lidar measurements of the chemical fluxes of Na and Fe would provide considerable insight into the diurnal variations of mesospheric \( \text{O}_2 \), \( \text{O}_3^* \), \( \text{NO}^+ \) and photoionization and their impact on metal transport. Our calculations of the turbulence-induced transport were made using a fixed value of 50 m/s for \( k_{zz} \) and by assuming that the intrinsic temperature spectrum was proportional to \( T^{-11/2} \). Although the results are not particularly sensitive to the shape of the turbulence spectrum, the predictions could be improved if more realistic models for the intrinsic temperature spectrum could be obtained. The predictions could also be improved by employing a more realistic profile for \( k_{zz} \) that was obtained from measurements or a wave-parameterization scheme.

Appendix A: Chemical Transport of Mesospheric Na and Fe

In the following, we adhere to the numbering scheme for the key Na reactions and their rates, which are tabulated in Table 1 of Plane et al. (2015). However, several of the reaction rates involving Na compounds have recently been updated, and these are summarized in Table 1 of this paper. Na is depleted by reacting with \( \text{O}_3 \) to form \( \text{NaO} \), which then reacts rapidly with \( \text{O} \) to form Na. In this way most of the \( \text{NaO} \) is recycled back to atomic Na. However, \( \text{NaO} \) also reacts with \( \text{H}_2 \) and \( \text{H}_2\text{O} \) to form \( \text{NaOH} \). \( \text{NaOH} \) can be recycled back to Na via several processes. It can also react with \( \text{CO}_2 \) to form the stable reservoir \( \text{NaHCO}_3 \) [Plane et al., 2015; Gómez Martín et al., 2015]. We assume that once \( \text{NaHCO}_3 \) is formed, the concomitant Na is permanently tied up in this reservoir, which readily forms the dimer and polymerizes with other meteoric debris to form meteoric smoke particles. Although \( \text{NaHCO}_3 \) can also be photolyzed or react with H to recycle Na, these processes are relatively slow compared to dimerization and polymerization and so to simplify the equations we neglect them.

Na is also depleted by reacting with \( \text{O}_2 \) to form \( \text{NaO}_2 \) which is then rapidly converted to Na by reacting with O. Above 95 km Na reacts with \( \text{O}_2^* \) and \( \text{NO}^+ \) to form Na and during the day Na can be photoionized. Because direct recombination is slow, \( \text{Na}^+ \) is converted back to Na by a series of reactions, which lead to the formation of the cluster ions \( \text{Na}_2\text{N}_2^+ \), \( \text{Na}_2\text{CO}_2^+ \), \( \text{Na}_2\text{H}_2\text{O}^+ \) and \( \text{NaO}^+ \) followed by dissociative recombination. The direct injection of \( \text{Na}^+ \) by meteoric ablation below 100 km is small and so we assume \( M_{\text{Na}^+} = 0 \). The relevant net chemical production and loss rates are

\[
\begin{align*}
Q_{\text{Na}} & = (k_3[\text{O}]+k_5[\text{O}_3]+k_7[\text{H}_2]+J_{31})[\text{NaO}]+J_{32}[\text{NaO}_2]+(k_7[\text{H}]+J_{33})[\text{NaOH}] + \omega_{\text{Na}^+}[\text{Na}^-] - (k_1[\text{O}_3]+k_{10}[\text{O}_2][\text{M}]+k_{20}[\text{O}^+]+k_{21}[\text{NO}^+]+J_{35})[\text{Na}] \\
Q_{\text{NaO}} & = k_1[\text{O}_3][\text{Na}]+k_{11}[\text{O}][\text{NaO}_2] - (k_2[\text{O}]+k_3[\text{O}_3]+k_4[\text{H}_2]+k_5[\text{H}_3]+k_6[\text{H}_2\text{O}]+k_7[\text{O}_3]+J_{31})[\text{NaO}] \\
Q_{\text{NaO}_2} & = k_{10}[\text{O}_2][\text{M}][\text{Na}]+k_2[\text{NaO}][\text{O}_3] - (k_{11}[\text{O}]+J_{32})[\text{NaO}_2] \\
Q_{\text{NaOH}} & = (k_4[\text{H}_2]+k_6[\text{H}_2\text{O}])[\text{NaO}] - (k_7[\text{H}]+k_8[\text{CO}_2][\text{M}]+J_{33})[\text{NaOH}] \\
Q_{\text{Na}^+} & = (k_{20}[\text{O}^2]+k_{21}[\text{NO}^+]+J_{35})[\text{Na}]+(k_{26}[\text{O}]+k_{28}[\text{O}_2])[\text{NaO}^+] - (k_{22}[\text{N}_2][\text{M}][\text{Na}^-] = (k_{20}[\text{O}^2]+k_{21}[\text{NO}^+]+J_{35})[\text{Na}] - \omega_{\text{Na}^+}[\text{Na}^-] \\
Q_{\text{Na}_2\text{N}_2^+} & = k_{22}[\text{N}_2][\text{M}][\text{Na}^-]+k_{27}[\text{N}_2][\text{NaO}^-] - (k_{24}[\text{H}_2\text{O}]+k_{24}[\text{CO}_2]+k_{25}[\text{O}])[\text{Na}_2\text{N}_2^+] \\
Q_{\text{Na}_2\text{CO}_2^+} & = k_{25}[\text{O}][\text{Na}_2\text{N}_2^+] - (k_{26}[\text{O}]+k_{27}[\text{N}_2]+k_{28}[\text{O}_2])[\text{NaO}^+] \\
Q_{\text{Na}_2\text{H}_2\text{O}^+} & = k_{24}[\text{H}_2\text{O}][\text{Na}_2\text{N}_2^+]-k_{29}[\text{e}^-][\text{Na}_2\text{H}_2\text{O}^+] \\
Q_{\text{NaH}_2\text{O}^+} & = k_{24}[\text{H}_2\text{O}][\text{Na}_2\text{N}_2^+]-k_{29}[\text{e}^-][\text{Na}_2\text{H}_2\text{O}^+].
\end{align*}
\]
Because the dominant loss reactions for intermediate species NaO, NaO$_2$, NaOH, Na-N$_2^+$, Na-CO$_2^+$, Na-H$_2$O$^+$, and NaO$^+$ in the region 85–100 km are fast, the lifetimes of these species are relatively short compared to the timescale of vertical transport:

$$\tau_{\text{NaO}} = \frac{1}{k_2[O]} = 10 \text{ ms}$$
$$\tau_{\text{NaO}_2} = \frac{1}{k_{11}[O]} = 0.5 \text{ s}$$
$$\tau_{\text{NaOH}} = \frac{1}{k_7[H] + J_{33}} = 5 \text{ min at night} - 1 \text{ min at day}$$
$$\tau_{\text{Na-N}_2^+} = \frac{1}{k_{32}[O]} = 5 \text{ ms}$$
$$\tau_{\text{NaO}^+} = \frac{1}{k_{26}[O]} = 0.2 \text{ s}$$
$$\tau_{\text{Na-CO}_2^+} = \frac{1}{k_{29}[e^-]} = 8.5 \text{ min at night} - 0.25 \text{ s at day}$$
$$\tau_{\text{Na-H}_2O^+} = \frac{1}{k_{29}[e^-]} = 8.5 \text{ min at night} - 0.25 \text{ s at day}.$$  

and so we assume that these species are in chemical equilibrium. The Na$^+$ lifetime is about 20 h at 100 km, about 3 h at 95 km, and only a few minutes at 90 km [Cox and Plane, 1998]. Na$^+$ is in chemical equilibrium certainly below ~95 km. However, to simplify calculations, we assume that Na$^+$ is in chemical equilibrium up to 100 km. In this case we have

$$\mathcal{Q}_{\text{NaO}} = 0$$
$$\mathcal{Q}_{\text{NaO}_2} = 0$$
$$\mathcal{Q}_{\text{NaOH}} = 0$$
$$\mathcal{Q}_{\text{Na-N}_2^+} = 0$$
$$\mathcal{Q}_{\text{NaO}^+} = 0$$
$$\mathcal{Q}_{\text{Na-CO}_2^+} = 0$$
$$\mathcal{Q}_{\text{Na-H}_2O^+} = 0$$

and

$$\mathcal{Q}_{\text{Na}} = -k_6[\text{CO}_2][\text{M}][\text{NaOH}]$$
$$\mathcal{Q}_{\text{Na}^+} = 0$$

where

$$[\text{NaOH}] = \frac{k_4[H_2] + k_6[H_2O]}{(k_7[H] + k_8[\text{CO}_2][\text{M}] + J_{33})} [\text{NaO}]$$

$$[\text{NaO}] = \frac{(k_1[O_3] + \frac{k_{11}[O]}{k_{11}[O] + J_{32}} k_{10}[O_2][\text{M}]) [\text{Na}]}{\left( k_2[O] + \frac{k_3 + J_{33}k_x}{k_3[O] + J_{32}} \right) [O_3] + k_4[H_2] + k_5[H_2] + k_6[H_2O] + J_{31}}$$

$$[\text{Na}^+] \equiv \frac{k_{20}[O_2^+] + k_{21}[\text{NO}^+] + J_{35}}{k_{20}[O_2^+]} [\text{Na}].$$  

Notice that according to (A4), Na is also in chemical equilibrium above about 90 km where the loss to the stable reservoir NaHCO$_3$ (R8 in Table 1) is negligible. Although we employed the continuity equation for neutral species, below 100 km the neutral atmospheric density is large enough that the motions of ions are equal to the motions of the neutral atmosphere.
In the spectral domain, the perturbed net production/loss rates for the neutral and ionic Na species are given by (12)

\[
Q_{Na}^{\prime}(\omega) - \omega_M [Na(\omega)] = \frac{i \omega}{\omega_{Na} + \omega_M + i \omega} \left[ \left( T_{Na} - \frac{(M_{Na} + \theta_{Na})}{T} \right) - \left( \frac{\theta_{Na}}{\partial z} + \frac{M_{Na} + \theta_{Na}}{T} \right) T^\prime(\omega) + \frac{1}{i \omega} \right]
\]

(A5)

\[
Q_{Na}^{\prime}(\omega) = \frac{i \omega}{\omega_{NaO} + i \omega} \left[ \left( T_{NaO} - \frac{(M_{NaO} + \theta_{NaO})}{T} \right) T^\prime(\omega) \right] - \frac{1}{i \omega} \left( k_{21}[O] + k_{33}[O_3] + k_{34}[H_2] + J_{31} \right) Q_{Na}^{\prime}(\omega)
\]

\[
Q_{NaO}^{\prime}(\omega) = \frac{i \omega}{\omega_{NaO} + i \omega} \left[ \left( T_{NaO} - \frac{(M_{NaO} + \theta_{NaO})}{T} \right) T^\prime(\omega) \right] + \frac{1}{i \omega} \left( k_{21}[O] + k_{33}[O_3] + k_{34}[H_2] + J_{31} \right) Q_{Na}^{\prime}(\omega)
\]

\[
Q_{NaOH}^{\prime}(\omega) = \frac{i \omega}{\omega_{NaOH} + i \omega} \left[ \left( T_{NaOH} - \frac{(M_{NaOH} + \theta_{NaOH})}{T} \right) T^\prime(\omega) \right] + \frac{1}{i \omega} \left( k_{21}[O] + k_{33}[O_3] + k_{34}[H_2] + J_{31} \right) Q_{Na}^{\prime}(\omega)
\]

Equation (12) was derived by only considering the chemically induced perturbations in C (see discussion preceding equation (9)). In deriving (A5) from (12) we also included the chemically induced perturbations of Na, Na+, NaO, NaOH, and O3 because these species are strongly dependent on chemistry. By solving the system of equations given in (A5) we obtain

\[
Q_{Na}^{\prime}(\omega) = \frac{i \omega}{\omega_{Na} + i \omega} \left[ \left( T_{Na} - \frac{(M_{Na} + \theta_{Na})}{T} \right) T^\prime(\omega) \right] - \frac{1}{i \omega} \left( k_{21}[O] + k_{33}[O_3] + k_{34}[H_2] + J_{31} \right) Q_{Na}^{\prime}(\omega)
\]

(A6)

where

\[
\omega_{Na} = -T_{Na}/[Na] = k_{1}[O_3] + k_{10}[O_2] [M] + k_{20}[O_2] + k_{21}[NO^+] + J_{35}
\]

\[
\sigma_{Na} = -Q_{Na}/[Na] = k_3[CO_2][M][NaOH]/[Na] = \omega_M
\]

\[
\omega_{Na} + \omega_{Na} = \tau_{Na}/[Na] = M_{Na}/[Na] = k_1[O_3] + k_{10}[O_2] [M] + k_{20}[O_2] + k_{21}[NO^+] + J_{35}
\]

\[
\omega_{Na} = \frac{k_{24}[H_2O] + k_{24}[CO_2] + k_{29}[e^-]}{k_{24}[H_2O] + k_{24}[CO_2] + k_{29}[e^-] + k_{25}[O] + k_{26}[O_3] + k_{26}[O_3] + k_{26}[O_2] + k_{26}[O_2]}
\]

\[
\omega_{Na} = k[O] + k_3[O_3] + k_{4}[H_2] + k_5[H] + k_6[H_2O] + k_7[O_3] + J_{31} + k_2[O]^+ \omega_{Na} = k_{11}[O] + J_{32} + k_7[O] + \omega_{Na}
\]

\[
\omega_{Na} = k_{11}[O] + J_{32} + k_7[O] + \omega_{Na}
\]
By combining this result with (14), the Na chemical transport velocity is as follows:

\[
\bar{w}_{\text{Na,chem}} \equiv V_{\text{Na}}(0) - \frac{[\text{Na}^+]_0}{[\text{Na}]} V_{\text{Na}^-} \left[ (\alpha_{\text{Na}^+} - \frac{\beta}{[\text{C}]} (M_C + Q_C) / [\text{C}] \right] \\
- \frac{[\text{NaOH}]}{[\text{Na}]} \left[ \frac{k_{23}^\text{[H}_2\text{O}]}{\alpha_{\text{NaOH}}} V_{\text{NaOH}}(0) + \frac{k_{35}^\text{[CO}_2\text{]} [\text{M}]}{\alpha_{\text{NaOH}}} V_{\text{NaOH}}(0) \right] \tag{A8}
\]

where

\[
V_C(x) = S_T(x) \left( \frac{[\omega_C M_C - \beta (M_C + Q_C) / [C]]}{N} \right) + \frac{g}{N} \left( \frac{\omega_C}{\epsilon^2 \omega} \frac{\omega_C}{\sqrt{\epsilon^2 - \omega^2}} + \frac{M_C / [C]}{\sigma_{\epsilon = \text{const}, H_C}} \right) \\
+ S_{HF}(x) \left( \frac{\omega_{ac} [\omega_C M_C - \beta (M_C + Q_C) / [C]]}{\omega_C + (M_C + Q_C) / [C]} \right) \frac{w_T}{T} \\
+ S_{HF}(x) \left( \frac{\omega_{ac} [\omega_C M_C - \beta (M_C + Q_C) / [C]]}{\omega_C + (M_C + Q_C) / [C]} \right) \frac{w_T}{T}
\]

and

\[
S_T(x) = \frac{1}{B_T} \left( \frac{1}{2} \int_{0}^{\infty} \frac{e^{x/2} (\epsilon_{HF} / \epsilon) d\epsilon}{(\epsilon^2 + x^2)} \right) \]

\[
S_T(0) = 1 \\
S_{HF}(x) = \frac{1}{w_T} \left( \frac{1}{2} \int_{0}^{\infty} \frac{e^{x/2} (\epsilon_{HF} / \epsilon) d\epsilon}{(\epsilon^2 + x^2)} \right) \\
S_{HF}(0) = 0.
\]

and

\[
\pi_{\text{Na}} = 4.12 - 3\beta \\
\alpha_{\text{Na}^+} = (2.2 - \beta) + \frac{0.7 k_{23}^\text{[CO}_2\text{]} [\text{M}]}{\alpha_{\text{Na}^+}} - \frac{J_{35}^\text{[NO}_2\text{]}}{M_{O_2}} + \frac{J_{35}^\text{[NO}_2\text{]}}{M_{O_2}} + \frac{J_{35}^\beta}{\alpha_{\text{NaOH}}} \tag{A9}
\]

\[
\alpha_{\text{NaOH}} = \frac{[\text{NaOH}]}{[\text{NaOH}]} \left( \frac{k_{20}^\text{[H}_2\text{O}]}{\alpha_{\text{NaOH}}} + \frac{k_{35}^\text{[CO}_2\text{]} [\text{M}]}{\alpha_{\text{NaOH}}} (4.12 - \beta) + \frac{J_{35}^\beta}{\alpha_{\text{NaOH}}} \right)
\]

Note when using (A9) to evaluate \( V_{\text{Na}}(0) \), the parameters \( \pi_{\text{Na}} \) and \( \pi_{\text{Na}} \) should be employed instead of \( \alpha_{\text{Na}^+} \) and \( \alpha_{\text{Na}^-} \). The chemical transport of Na comprises three terms, which are related to the chemical perturbations in Na, Na\(^+\), and NaOH. Notice that the velocity function \( V_C \) has the same form as the chemical transport velocity given by (15), which was derived for the special case where only the species C exhibited chemically induced density fluctuations. For nonmeteoric species that are in chemical equilibrium, \( V_C \) simplifies to

\[
V_C(x) = S_T(x) \frac{\omega_{ac} [\omega_C M_C - \beta (M_C + Q_C) / [C]]}{N} \frac{g (T)}{N} \frac{w_T}{T} + S_{HF}(x) \frac{\omega_{ac} [\omega_C M_C - \beta (M_C + Q_C) / [C]]}{N} \frac{w_T}{T}.
\]

The key reactions for Fe between 85 and 100 km and their rates are summarized in Table 3 of Plane et al. [2015]. Several of the reaction rates have recently been updated, and these are tabulated in Table 2 of this paper. At the lower altitudes Fe is depleted by reacting with O\(_3\) to form FeO, which then reacts rapidly with O to form Fe. Analogous to Na, most of the FeO is recycled back to atomic Fe. However, FeO also reacts with H\(_2\)O to form Fe(OH)\(_2\), with O\(_2\) to form FeO\(_3\), and with O\(_3\) to form FeO\(_2\), which, in turn, reacts with O\(_3\) to form FeO\(_2\). FeO\(_2\) is also rapidly recycled back to FeO by reacting with O. FeO\(_3\) and Fe(OH)\(_2\) react with H to form FeOH, which, in turn, can form the stable dimer or react with H to form Fe. Because the dominant loss
reactions for FeO, FeO$_2$, FeO$_3$, Fe(OH)$_2$, and FeOH are fast and the lifetimes of these species are relatively short compared to the timescale of vertical transport.

\[
\tau_{\text{FeO}} = \frac{1}{k_2[O]} \approx 25 \text{ ms}
\]

\[
\tau_{\text{FeO}_2} = \frac{1}{k_3[O]} \approx 0.25 \text{ s}
\]

\[
\tau_{\text{FeO}_3} = \frac{1}{k_7[O]} \approx 15 \text{ min}
\]

\[
\tau_{\text{Fe(OH)}_2} = \frac{1}{k_{10}[H]} \approx 2.5 \text{ min}
\]

\[
\tau_{\text{FeOH}} = \tau_{\text{Fe(OH)}_2} = \frac{1}{(k_{12a} + k_{12b})[H] + J_{32}} \approx 10 \text{ h at night} \approx 3 \text{ min at day},
\]

we assume that all of these species are in chemical equilibrium. Above 95 km Fe reacts with O$_2^+$ and NO$^+$ to form Fe$^+$ and during the day Fe can be photoionized. Although Fe$^+$ can be neutralized through direct recombination or through the formation of cluster ions and then dissociative recombination, these processes are very slow. The Fe$^+$ lifetime is several days above 85 km [Bones et al., 2015], so we may regard the ion as a stable Fe reservoir. The relevant net chemical production and loss rates are as follows:

\[
Q_{\text{FeO}} = k_2[\text{FeO}][O] + k_{12a}[\text{FeOH}][H] + J_{32}[\text{FeOH}]
- k_1[\text{Fe}][O_3] - k_{19}[\text{Fe}][O^+] - k_{19}[\text{Fe}][O_2^+] - J_{33}[\text{Fe}]
\]

\[
Q_{\text{FeO}_2} = k_1[\text{Fe}][O_3] + k_3[\text{FeO}_2][O] + k_{12b}[\text{FeOH}][H]
- k_2[\text{FeO}][O] - k_3[\text{FeO}][O_3] - k_4[\text{FeO}][O_2][M] - k_5[\text{FeO}][H_2O][M]
\]

\[
Q_{\text{FeO}_3} = k_3[\text{FeO}][O_3] + k_7[\text{FeO}_3][O] - k_3[\text{FeO}_2][O] - k_6[\text{FeO}_2][O_3]
\]

\[
Q_{\text{Fe(OH)}_2} = k_8[\text{FeO}_3][H_2O] + k_9[\text{FeO}][H_2O][M] - k_{10}[\text{Fe(OH)}_2][E]
\]

\[
Q_{\text{FeOH}} = k_{10}[\text{Fe(OH)}_2][H] + k_{11}[\text{FeO}_3][H]
- (k_{12a} + k_{12b})[\text{FeOH}][H] - k_{13}[\text{FeOH}]^2 - J_{32}[\text{FeOH}],
\]

where

\[
\overline{Q}_{\text{FeO}} = 0
\]

\[
\overline{Q}_{\text{FeO}_2} = 0
\]

\[
\overline{Q}_{\text{FeO}_3} = 0
\]

\[
\overline{Q}_{\text{Fe(OH)}_2} = 0
\]

\[
\overline{Q}_{\text{FeOH}} = 0
\]

and

\[
\overline{Q}_{\text{FeO}} = 0
\]

\[
\overline{Q}_{\text{FeO}_2} = 0
\]

\[
\overline{Q}_{\text{FeO}_3} = 0
\]

\[
\overline{Q}_{\text{Fe(OH)}_2} = 0
\]

\[
\overline{Q}_{\text{FeOH}} = 0
\]
\[ \mathcal{Q}_F = - \left( k_{13} \left[ FeOH \right]^2 + k_{18} \left[ NO^+ \right] [Fe] + k_{19} \left[ O_2^+ \right] [Fe] + J_{33} [Fe] \right) \]

where

\[ [FeOH] = \frac{(k_{12a} + k_{12b}) [H] + J_{32}}{2k_{13}} \left\{ -1 + \sqrt{1 + 4k_{10} \left[ Fe(OH)_2 \right] [H] + k_{11} \left[ FeO_2 \right] [H]} \right\} \]

\[ [Fe(OH)_2] = k_8 \left[ FeO_3 \right] [H_2O] + k_9 \left[ FeO \right] [H_2O] [M] \]

\[ [FeO] = \frac{1}{k_{10} [H] \left( k_2 [O] - k_3 [O] - \frac{k_2 k_8 [O]}{k_5} - k_1 \frac{k_3 [O]^2}{k_2 [O]} - k_4 [O_2] [M] \right)} k_{13} [O_3] [Fe] \]

\[ [FeO_2] = \frac{1}{k_{12} [O] - k_3 [O] - \frac{k_2 k_6 [O]}{k_5} - k_1 \frac{k_3 [O]^2}{k_2 [O]} - k_4 [O_2] [M]} k_{13} [O_3] [Fe] \]

\[ [FeO_3] = \frac{1}{k_{12} [O] - k_3 [O] - \frac{k_2 k_6 [O]}{k_5} - k_1 \frac{k_3 [O]^2}{k_2 [O]} - k_4 [O_2] [M]} k_{13} [O_3] [Fe] \]

\[ \alpha_{Fe,chem} = \alpha_{Fe} \frac{\mathcal{W}_{Fe,chem}}{V_{Fe}(0)} = k_{13} \left[ FeOH \right]^2 + k_{18} [NO^+] + k_{19} \left[ O_2^+ \right] + J_{33} \]

\[ \alpha_{Fe} = \frac{J_{33}}{\alpha_{Fe}} - 2 \beta \]

\[ \alpha_{FeOH} = \alpha_{Fe} \]

\[ \alpha_{FeO_2} = \alpha_{Fe} \]

\[ \alpha_{Fe(OH)_2} = \alpha_{Fe} \]

\[ \alpha_{Fe(OH)_3} = \alpha_{Fe} \]

\[ \alpha_{Fe(OH)} = 1 - \frac{\alpha_{FeOH}}{\alpha_{Fe}} \]

\[ \alpha_{Fe(OH)_2} = 1 - \frac{\alpha_{FeOH}}{\alpha_{Fe}} \]

\[ \alpha_{Fe(OH)_3} = 1 - \frac{\alpha_{FeOH}}{\alpha_{Fe}} \]

\[ \alpha_{Fe(OH)} = 1 - \frac{\alpha_{FeOH}}{\alpha_{Fe}} \]

\[ \alpha_{Fe(OH)_2} = 1 - \frac{\alpha_{FeOH}}{\alpha_{Fe}} \]

\[ \alpha_{Fe(OH)_3} = 1 - \frac{\alpha_{FeOH}}{\alpha_{Fe}} \]

\[ \alpha_{Fe(OH)} = 1 - \frac{\alpha_{FeOH}}{\alpha_{Fe}} \]

\[ \alpha_{Fe(OH)_2} = 1 - \frac{\alpha_{FeOH}}{\alpha_{Fe}} \]

\[ \alpha_{Fe(OH)_3} = 1 - \frac{\alpha_{FeOH}}{\alpha_{Fe}} \]

\[ \alpha_{Fe(OH)} = 1 - \frac{\alpha_{FeOH}}{\alpha_{Fe}} \]

\[ \alpha_{Fe(OH)_2} = 1 - \frac{\alpha_{FeOH}}{\alpha_{Fe}} \]

\[ \alpha_{Fe(OH)_3} = 1 - \frac{\alpha_{FeOH}}{\alpha_{Fe}} \]

\[ \alpha_{Fe(OH)} = 1 - \frac{\alpha_{FeOH}}{\alpha_{Fe}} \]

\[ \alpha_{Fe(OH)_2} = 1 - \frac{\alpha_{FeOH}}{\alpha_{Fe}} \]

\[ \alpha_{Fe(OH)_3} = 1 - \frac{\alpha_{FeOH}}{\alpha_{Fe}} \]

\[ \alpha_{Fe(OH)} = 1 - \frac{\alpha_{FeOH}}{\alpha_{Fe}} \]

\[ \alpha_{Fe(OH)_2} = 1 - \frac{\alpha_{FeOH}}{\alpha_{Fe}} \]

\[ \alpha_{Fe(OH)_3} = 1 - \frac{\alpha_{FeOH}}{\alpha_{Fe}} \]
Note when using (A9) to evaluate \( V_{\text{rel}}(0) \), the parameters \( \alpha_{\text{Fe}} \) and \( \alpha_{\text{Fe}} \) should be employed instead of \( \alpha_{\text{Fe}} \).

The chemistries of K and Ca are similar to Na and the chemistry of Mg is similar to Fe [e.g., Plane et al., 2015]. Therefore, the expressions for the chemical transport of K and Ca are similar to (A8), while for Mg the transport is similar to (A16). The expressions for K, Ca, and Mg transport can be derived using the approaches outlined above.

Appendix B: Intrinsic Frequency Spectra of Turbulence

To estimate the scale factors \( S_{\text{Turb}} \) and \( S_{\text{Turb}}' \) we assume that the one-sided intrinsic frequency spectrum of the vertical wind fluctuations, caused by turbulence, is proportional to \( \omega^{-P} \) between the frequencies \( \omega_o \) and \( \omega_i \) where \( 1 < p \) and \( \omega_b < \omega_i \).

\[
F_{\text{Turb}}(\omega) = \begin{cases} 
2\pi(p-1)\omega^2_{\text{Turb}} & \omega_o \leq \omega \leq \omega_i \\
0 & \text{otherwise}
\end{cases}
\]

where \( \omega_o = 2\pi/\tau_o \).

To determine \( \omega_b \), we compute the temperature variance from the vertical wind spectrum by noting that

\[
T' = -\frac{N^2}{g} \int_{-\infty}^{\infty} w^2 \tau \, d\tau,
\]

and equating the result to the temperature variance derived from spatial spectrum of the relative temperature fluctuations

\[
\left( \frac{T'_{\text{Turb}}}{T} \right)^2 = \frac{N^4}{g^2} \int_{\omega_o}^{\omega_i} \frac{F_{\text{Turb}}(\omega)}{\omega^2} \, d\omega
\]

where the right-hand side of (B3) comes from (32) and (33). By assuming that \( (\omega_o/\omega)^{P-1} \ll 1 \) we obtain

\[
\omega_b = N \sqrt{\frac{(p-1)}{2(p+1)}}
\]

\[
\tau_o = \tau_b \sqrt{\frac{2(p+1)}{(p-1)}}
\]

When the intrinsic vertical wind spectrum is proportional to \( \omega^{-P} \), the intrinsic temperature spectrum is proportional to \( \omega^{-(p+2)} \), and the heat flux distribution is proportional to \( \omega^{-(p+1)} \) so that

\[
F_{\text{Turb}}'(\omega) = \begin{cases} 
2\pi(p+1)\left( \frac{T'_{\text{Turb}}}{\omega} \right)^2 & \omega_o \leq \omega \leq \omega_i \\
0 & \text{otherwise}
\end{cases}
\]

\[
HF_{\text{Turb}}(\omega) = \begin{cases} 
2\pi p \omega^2_{\text{Turb}} F_{\text{Turb}}'(\omega) & \omega_o \leq \omega \leq \omega_i \\
0 & \text{otherwise}
\end{cases}
\]

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References


