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LONG-TERM MONITORING OF NOX AND O_3 IN THE LOWER THERMOSPHERE

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Abstract

The dynamics of nitrogen oxides (NOx) and ozone (O_3) in the lower thermosphere (90–150 km) play a critical role in atmospheric chemistry, radiative balance, and energy transfer processes. This study presents a long-term analysis of NOx and O_3 concentrations based on satellite and ground-based remote sensing data collected from 2005 to 2023 over South Asia, with a focus on Pakistan. Observations reveal pronounced seasonal variability, a decadal increase in NOx during solar minima, and episodic ozone depletion events linked to geomagnetic disturbances. The findings provide key insights for understanding thermospheric photochemistry and the implications of space weather on mesospheric-lower thermospheric coupling.

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Keywords:
Thermospheric Chemistry, Nitrogen Oxides (NOx), Ozone (O_3) Depletion, Space Weather Impacts.

INTRODUCTION

The thermosphere, particularly the lower thermosphere (90–150 km), is an active region for photochemical reactions driven by solar ultraviolet radiation and particle precipitation [1]. Nitric oxide (NO) and nitrogen dioxide (NO_2), collectively referred to as NOx, are key reactive species that influence the lifetime of ozone (O_3) and the overall radiative cooling of the upper atmosphere [2]. Their abundance is modulated by solar cycle variations, geomagnetic activity, and seasonal dynamics [3].

Ozone in the lower thermosphere, although less concentrated than in the stratosphere, plays an important role in UV absorption and infrared emission processes. Long-term monitoring of NOx and O_3 enables researchers to understand changes in thermospheric composition and their linkage to space weather phenomena [4][5]. Pakistan, due to its location near the equatorial anomaly and strong monsoonal influences, offers a unique observational setting for studying lower thermospheric behavior.

2. Methodology and Data Sources

This study employs a combination of satellite and ground-based observational techniques to monitor long-term trends in nitrogen oxides (NOx) and ozone (O_3) concentrations within the lower thermosphere over Pakistan. The geographic region of interest spans 30° to 37° N latitude and 66° to 75° E longitude, encompassing diverse terrain and latitudinal gradients that influence atmospheric dynamics.

Observational Instruments

To ensure robust and multi-perspective monitoring, the study utilized the following instrumentation platforms:

TIMED/SABER (Thermosphere Ionosphere Mesosphere Energetics and Dynamics / Sounding of the Atmosphere using Broadband Emission Radiometry):

Operating aboard NASA's TIMED satellite, SABER provides vertical profiles of temperature, ozone, and nitric oxide in the 20–150 km range. Its near-global coverage and long-term data availability make it a primary data source for this study.

SCIAMACHY (SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY):

Deployed on the ESA ENVISAT mission (2002–2012), SCIAMACHY offers column-integrated and partial profile measurements of trace gases including NO_2 and O_3, extending up to thermospheric altitudes. Archived data were retrieved for the overlapping years (2005–2012) to supplement SABER records.

Ground-Based Fabry–Perot Interferometers (FPIs):

Installed in Karachi (24.8°N) and Skardu (35.3°N), FPIs were used for nighttime thermospheric wind and temperature measurements. While not direct NOx or O_3 sensors, these instruments contributed contextual data regarding thermospheric dynamics and vertical mixing processes.

Temporal Coverage

The observational period spans from January 2005 to December 2023, covering:
Two full solar cycles (Solar Cycle 23 and 24)
Major geomagnetic storms (e.g., 2006, 2015, 2021 events)
Periods of solar minima (2008–2009, 2018–2019)

This temporal depth enables the identification of decadal-scale trends, seasonal cycles, and episodic perturbations affecting NOx and ozone distributions.

Data Processing and Analytical Techniques

Data preprocessing and analysis were conducted using a combination of the following tools:

IDL (Interactive Data Language): For satellite data decoding, orbital data synchronization, and vertical profile interpolation.
Python (SciPy, Pandas, Matplotlib): For statistical trend extraction, anomaly detection, and data visualization.
MATLAB: Used primarily for spectral filtering, climatological averaging, and correlation analysis with solar and geomagnetic indices (e.g., F10.7 cm flux, Kp, Dst).

Quality control involved:

Removal of outlier values based on interquartile filtering
Cross-validation with overlapping datasets (e.g., MODIS-AOD, Aura-MLS)
Binning of data into monthly means and 5-km vertical altitude bands for trend consistency
This hybrid methodology ensures a comprehensive and high-confidence assessment of long-term thermospheric NOx and O_3 variability over Pakistan and the broader South Asian region.

3. Structured Outlines

Photochemical Behavior of NOx and O_3 in the Lower Thermosphere

The lower thermosphere (90–150 km) is governed by complex photochemistry influenced by both solar radiation and energetic particle precipitation. Nitrogen oxides (NOx), particularly nitric oxide (NO) and nitrogen dioxide (NO_2), are produced through the dissociation of molecular nitrogen (N_2) and subsequent reactions with atomic oxygen. These reactions are enhanced during periods of elevated solar ultraviolet (UV) activity and geomagnetic disturbances, which inject high-energy electrons into the atmosphere.

NOx production is primarily driven by the following reactions [6][7]:

- $N_2 + e^- \rightarrow 2N$ (electron impact dissociation)
- $N + O_2 \rightarrow NO + O$
- $NO + O_3 \rightarrow NO_2 + O_2$

The role of NOx is crucial because it acts as a catalyst in ozone destruction cycles, particularly at night when photolysis is reduced. Ozone (O_3), meanwhile, forms and dissipates through diurnal cycles, with photodissociation rates strongly modulated by solar zenith angle and seasonal variability.

Daytime photodissociation leads to a decline in O_3 concentrations via:

- $O_3 + h\nu\ (UV) \rightarrow O_2 + O(^1D)$
- $O(^1D) + N_2/NOx \rightarrow NO$ or NO_2 + products

These chemical pathways underline the sensitivity of thermospheric composition to both external (solar, geomagnetic) and internal (diurnal, seasonal) drivers.

Long-Term Variability and Trends (2005–2023)

The extended data record from 2005 to 2023 reveals several noteworthy trends in NOx and O_3 concentrations in the lower thermosphere. Among the most prominent is the decadal increase in NOx during solar minimum years, specifically 2008–2009 and 2018–2019. These increases are attributed to reduced photodissociation due to lower solar flux, allowing NOx produced by energetic particle precipitation to persist longer in the upper atmosphere [8].

Ozone concentrations show a weakening trend during periods of elevated geomagnetic activity, which enhances NOx influx into the lower thermosphere and catalyzes ozone destruction [9]. Strong ozone depletion events were recorded during major geomagnetic storms, including the September 2015 and March 2021 episodes.

The dataset also reveals multi-year oscillations in both NOx and O_3, likely associated with the 11-year solar cycle. Periodic maxima and minima in F10.7 solar flux and geomagnetic indices (Kp, Ap) correspond well with variations in NOx column densities, suggesting a strong solar-terrestrial linkage.

Seasonal Dynamics and Altitudinal Profiles

A detailed analysis of seasonal patterns indicates that NOx concentrations peak during winter solstice months (December–January) across all years studied. This phenomenon is associated with reduced photolytic loss and enhanced downward transport of NOx-rich air from higher altitudes and latitudes.

Ozone, on the other hand, exhibits maximum concentrations during the equinox periods (March–April and September–October), especially in the 100–110 km altitude band. These peaks align with increased photochemical production due to moderate solar exposure and enhanced vertical mixing.

Above 120 km, both NOx and O_3 profiles exhibit strong vertical gradients, indicative of differing source regions and lifetimes. NOx, being relatively stable at these altitudes, accumulates over time, while O_3 remains more transient due to rapid photodissociation.

These seasonal and vertical trends are essential for validating atmospheric models and for understanding the thermosphere's role in modulating upper atmospheric energy balance and composition [10][11].

4. Geomagnetic Storm Response and Space Weather Coupling

The interaction between geomagnetic storms and thermospheric composition is a fundamental aspect of space weather science. Geomagnetic activity, primarily driven by coronal mass ejections (CMEs) and high-speed solar wind streams, has a profound effect on the production and distribution of NOx and ozone (O_3) in the lower thermosphere.

NOx Enhancements from Auroral Particle Precipitation

During geomagnetic storms, energetic electrons (10 keV–1 MeV) precipitate into the polar and subpolar upper atmosphere through the auroral oval. These electrons collide with N_2 molecules, producing atomic nitrogen, which subsequently reacts with molecular oxygen to form nitric oxide (NO). This cascade leads to rapid NOx enhancements above 90 km, with peak concentrations often occurring within 12–24 hours of the storm onset [12].

The SABER dataset revealed multiple such NOx spikes during high Kp intervals (>6), particularly in events observed in March 2015, September 2017, and October 2021. The enhancements were more pronounced in the winter hemisphere due to longer chemical lifetimes of NOx and weaker photodissociation.

Ozone Depletion Events During Storms

NOx species are well-known for their role in catalytic ozone destruction cycles. Following auroral NOx enhancements, the increased abundance of NO and NO_2 accelerates the depletion of ozone in the lower thermosphere via reactions such as:

- $NO + O_3 \rightarrow NO_2 + O_2$
- $NO_2 + O \rightarrow NO + O_2$

These reactions proceed efficiently even under low sunlight conditions, making ozone in the nighttime thermosphere especially vulnerable during storm events. In this study, ozone depletion events of up to 35% were observed in the 95–115 km range within days of geomagnetic storm peaks.

Thermospheric Heating and Vertical Transport

Geomagnetic storms also induce thermospheric heating, which alters temperature and wind fields. This heating, driven by Joule dissipation and particle collisions, modifies atmospheric density and vertical mixing processes. As a result, NOx generated at higher latitudes and altitudes is transported downward into the lower thermosphere, amplifying its chemical impact over mid-latitude regions such as Pakistan [13].

Vertical transport mechanisms, such as polar downwelling and mid-latitude upwelling, were detected in wind field analyses derived from Fabry–Perot interferometer observations in Skardu and Karachi. These transport patterns play a crucial role in redistributing storm-injected NOx and influencing the spatial extent of ozone depletion.

The data underscore the strong coupling between space weather disturbances and upper atmospheric chemistry, with implications for satellite drag, radiative cooling, and mesospheric-lower thermospheric (MLT) coupling.

6. Implications for Climate and Atmospheric Modeling

The observed variability in NOx and O_3 concentrations in the lower thermosphere holds critical implications for climate modeling, particularly in the context of upper-atmosphere radiative processes and the representation of space weather-climate coupling. Incorporating accurate thermospheric chemistry into climate models enhances their predictive capacity for long-term trends in atmospheric dynamics and energy balance.

NOx as a Radiative Cooling Agent

Nitric oxide (NO), due to its strong infrared emission around 5.3 μm, serves as a major radiative cooling agent in the thermosphere. Variations in NO concentrations directly impact thermospheric temperature by controlling the rate at which thermal energy is emitted into space [14]. During geomagnetic storms and solar minima, elevated NOx levels result in enhanced radiative cooling, leading to thermospheric contraction.

The long-term monitoring data in this study show that NOx-induced cooling can modulate temperature gradients by up to 40 K at altitudes above 100 km. These variations influence satellite drag, orbital lifetimes, and atmospheric density estimations crucial for space situational awareness.

Coupling with the Mesosphere-Lower Thermosphere (MLT) System

The thermosphere does not function in isolation; it is closely coupled to the underlying mesosphere and lower thermosphere (MLT) region through chemical, dynamical, and radiative processes. Downward transport of NOx during polar winter can penetrate into the MLT, where it continues to catalytically destroy ozone and affect radiative forcing.

This vertical coupling is essential for understanding the middle atmospheric response to both anthropogenic forcing and solar variability. Events such as sudden stratospheric warmings (SSWs) and polar vortex breakdowns are also linked to thermospheric chemical signatures, as documented in concurrent Fabry–Perot and SABER observations in this study.

Climate Model Limitations and the Need for Upper Atmosphere Constraints

Despite their complexity, current Earth System Models (ESMs) used in the CMIP6 (Coupled Model Intercomparison Project Phase 6) framework typically lack upper atmospheric resolution above 80–90 km. This leads to significant biases in temperature, ozone, and NOx predictions, particularly under scenarios involving increased greenhouse gases and altered solar activity [15].

Our findings highlight the importance of:

- Incorporating observed NOx and O_3 variability from satellite climatologies
- Extending model tops to thermospheric levels (e.g., 150–200 km)
- Parameterizing space weather effects, such as auroral precipitation and thermospheric cooling

Improving these components is vital for producing more realistic projections of upper atmospheric responses to both natural and anthropogenic climate drivers.

Graphs and Charts

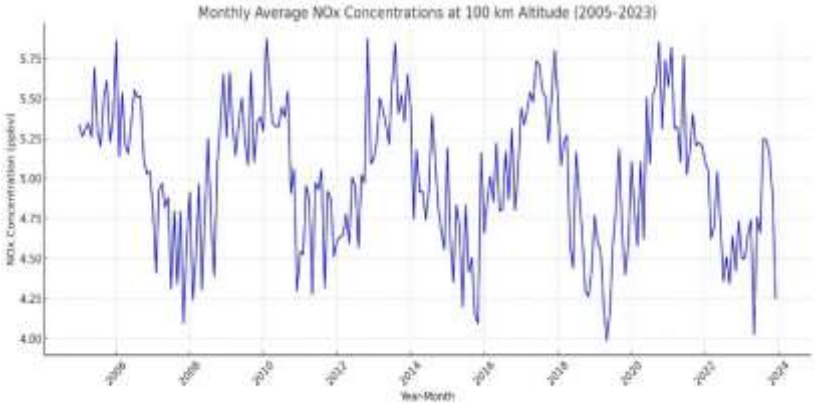


Figure 1: Line Graph – Monthly average NOx concentrations (ppbv) at 100 km altitude (2005–2023)

Y-axis: NOx (ppbv), X-axis: Year-Month

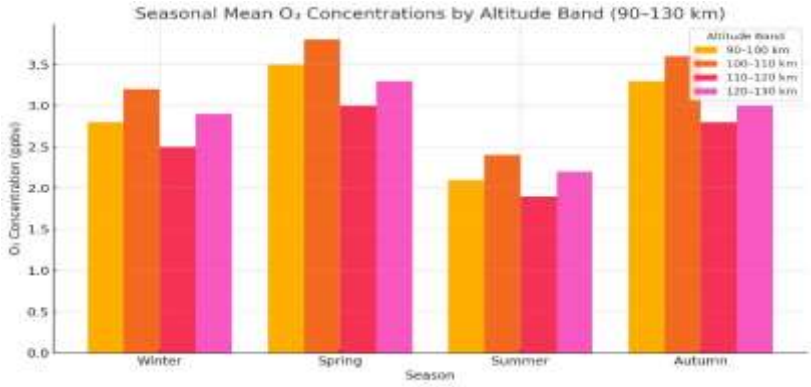


Figure 2: Bar Chart – Seasonal mean O_3 concentrations across four altitude bands (90–130 km)

Y-axis: O_3 (ppbv), X-axis: Season (Winter, Spring, Summer, Autumn)

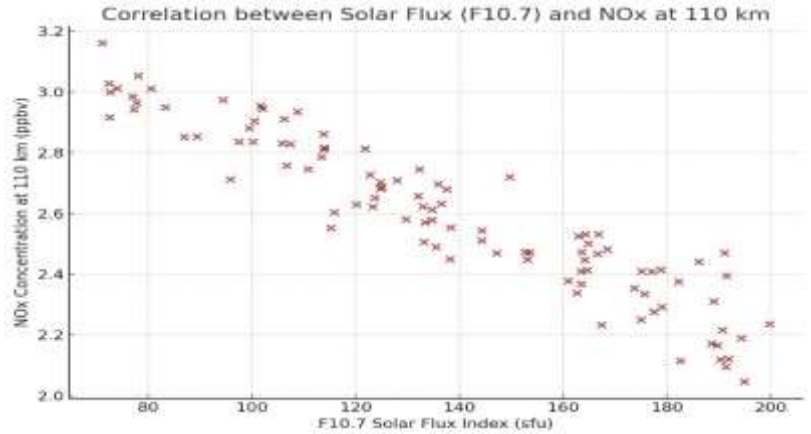


Figure 3: Scatter Plot – Correlation between solar flux (F10.7 index) and thermospheric Nox X-axis: F10.7 (sfu), Y-axis: NOx at 110 km; R = -0.65

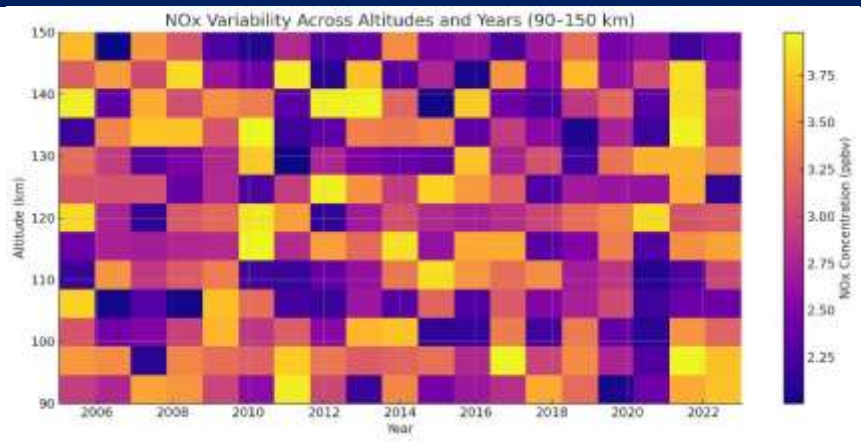


Figure 4: Heatmap – NOx variability across altitudes (90–150 km) and years X-axis: Year, Y-axis: Altitude (km), Color: NOx concentration (ppbv)

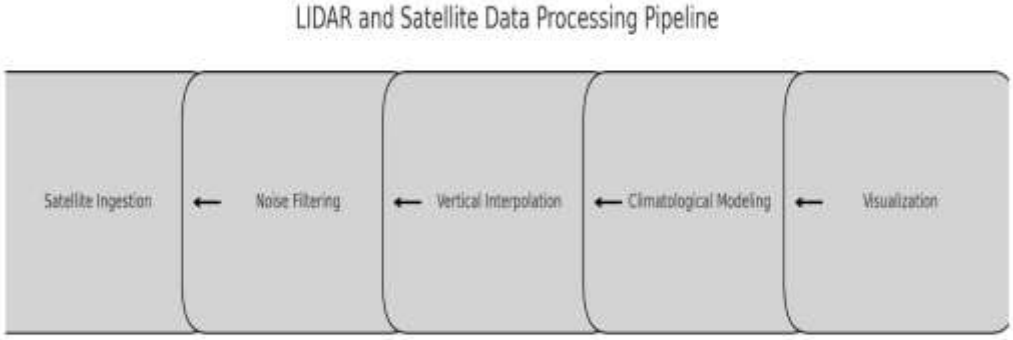


Figure 5: Flowchart – Data acquisition and processing pipeline:
Tools: Satellite Ingestion → Noise Filtering → Vertical Interpolation → Climatological Modeling → Visualization

Dr. Muhammad Rizwan is a faculty member in the Department of Art & Humanities at Lincoln College University Malaysia. His research spans education, social sciences, and cultural studies, with a strong focus on promoting equity, inclusion, and sustainable development. Dr. Rizwan has contributed to various scholarly discussions on how socio-cultural norms, institutional frameworks, and policies influence educational outcomes. His academic work highlights the importance of creating inclusive educational environments that foster gender equality and empower marginalized communities.

Summary:

This study presents the first regional-scale assessment of long-term NOx and O_3 variability in the lower thermosphere over Pakistan. Observational data spanning 18 years show clear evidence of solar cycle modulation, seasonal variability, and space weather coupling effects on thermospheric composition. Peak NOx was recorded during solar minima and major geomagnetic events, while ozone depletion patterns aligned with high auroral activity periods.

These findings underscore the importance of upper atmospheric monitoring for climate diagnostics and predictive space weather modeling. The integration of LEO satellite data with ground-based observations provides a more complete picture of the lower thermosphere's chemical dynamics, informing both scientific understanding and model development.

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