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Postprint: The Relationship Between O3 and VOCs, NOx in the Atmospheric Environment of Kuitun City

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Abstract

Taking Kuitun, a key city in the "Kuitun-Dushanzi-Wusu" region, as the study area, this study investigates the relationship between atmospheric O3 and VOCs and NOx in Kuitun City using monitoring data from 2013 to 2015. The results show that: O3 exceedances occurred for 33 days, 14 days, and 10 days in 2013, 2014, and 2015, respectively, with maximum daily average values of 0.457 mg · m ³, 0.396 mg · m ³, and 0.385 mg · m ³; O3 pollution was more severe in summer, with winter and summer O3 concentrations differing by nearly 2.5-fold; the diurnal variation of O3 concentration exhibited an inverted "U" -shaped distribution, with a peak occurring around 17:00; winter and summer VOCs concentrations differed by nearly 3-fold, and hourly VOCs values did not show a clear diurnal variation pattern; in winter, VOCs concentration was highest while O3 concentration was lowest, and the inverse relationship between them was not significant, but NOx concentration showed a symmetric inverse relationship with O3, indicating that O3 formation in Kuitun City during winter was in the NOx-sensitive regime rather than the VOCs-sensitive regime; in summer, the variation trends of VOCs and NOx were basically the same, O3 concentration levels were high, and both showed a symmetric inverse relationship, indicating that O3 formation in Kuitun City during summer was simultaneously in both the VOCs- and NOx-sensitive regimes, with O3 formation being alternately controlled by VOCs and NOx.

Full Text

Preamble

This study investigates the relationships among ozone (O), volatile organic compounds (VOCs), and nitrogen oxides (NO) concentrations in Kuitun City, Xinjiang, northwest China. The analysis is based on environmental monitoring data collected during 2013–2015.

1 Introduction

1.1 Study Area

Kuitun City is located in the northwestern part of the Tianshan Mountains' northern slope and serves as a key node on the northern route of the Silk Road Economic Belt. The city has a temperate continental arid climate characterized by scarce precipitation and abundant evaporation. In 2015, Kuitun' s industrial output reached 6.38×10 tons, with major industries including textiles, food processing, chemicals, papermaking, and building materials. The city experiences significant photochemical smog pollution, with 96.6% of days in 2015 meeting air quality standards. The average daily wastewater discharge was 1.48×10 tons, and the daily water consumption was 1.30×10 tons per day.

Photochemical smog pollution has become increasingly prominent in Kuitun, with VOCs and NO playing crucial roles in O formation. Since the 1950s, research has established the fundamental relationship between O , NO , and hydrocarbons in atmospheric chemistry. Previous studies have demonstrated that VOCs contribute significantly to O formation, with the relationship between O , NO , and VOCs showing complex nonlinear characteristics. The Empirical Kinetic Modeling Approach (EKMA) has been widely used to study these relationships.

1.2 Data and Methods

1.2.2 Data Processing VOCs, O , and NO concentrations were processed following standard quality control procedures. The VOCs data underwent noise reduction, baseline correction, and peak identification. Measurements below 0:00 with concentrations less than 4 ppbv were excluded from the 24-hour averages, with typical background values ranging from 2.8 to 5.2 ppbv. Data with relative standard deviation exceeding 30% were flagged and reviewed. Quality control measures included duplicate sample analysis and blank sample subtraction.

For O and NO data, the Signal-to-Noise Ratio (SNR) method was applied for quality assurance. The SNR threshold was set at 3:1 for peak identification, with baseline drift corrected using polynomial fitting. Data points deviating more than 3 from the mean were considered outliers and removed.

1.2.3 Photochemical Smog Mechanism The photochemical smog formation mechanism involves three key processes:

1. **NO photolysis**: NO absorbs solar radiation to form NO and atomic oxygen, which then reacts with O to form O . This establishes the fundamental photochemical equilibrium for O formation.

2. **VOCs oxidation**: VOCs react with hydroxyl radicals (HO·) to form peroxy radicals (RO ·), which convert NO to NO , promoting O accumulation.

3. **Radical cycling**: The interconversion between NO and NO , coupled with radical propagation reactions, sustains the photochemical chain reaction leading to O and PAN formation.

Table 1 presents the basic reaction mechanism of photochemical smog.

2 Results and Analysis

2.1 Basic Characteristics

During 2013–2015, O concentrations exceeded standards on 33, 14, and 10 days respectively, with maximum daily concentrations of 0.457, 0.396, and 0.385 mg · m ^{3}. The highest monthly average O concentrations occurred in summer (May–September), while the lowest values appeared in winter (November–January). Summer O concentrations were approximately 2.5 times higher than winter values.

[Figure 2: see original paper]

2.2 Monthly Variation

Monthly O concentrations showed a distinct seasonal pattern, with peak values in July and minimum values in January. The 2013 monthly average concentrations ranged from 0.038 to 0.327 mg · m ^{3}. In 2014–2015, the monthly patterns were similar, with peak concentrations of 0.148 and 0.154 mg · m ^{3} respectively.

[Figure 3: see original paper]

2.3 Diurnal Variation

The diurnal O concentration curve exhibited a typical "U-shaped" pattern. In January 2013, the average O concentration was 0.094 mg · m ^{3}, with no significant peak. In July 2013, the average concentration reached 0.457 mg · m ^{3}, with a pronounced peak between 16:00–17:00. The 24-hour O concentration analysis revealed that concentrations began rising after 13:00, peaked at 16:00–18:00, and then declined rapidly.

[Figure 4: see original paper]

[Figure 5: see original paper]

3 Relationship Analysis

3.1 Correlation Analysis

Statistical analysis revealed significant correlations among O , NO , and VOCs concentrations. In winter, high VOCs concentrations corresponded with low

O levels due to insufficient photochemical activity. In summer, VOCs and NO concentrations showed synchronous variation, with O reaching maximum values. The correlation coefficients between O and NO, and between O and VOCs, varied seasonally, indicating different controlling mechanisms.

[Figure 7: see original paper]

3.2 Photochemical Regime Analysis

The relationship between O, VOCs, and NO was further analyzed using the EKMA framework. The results indicated that Kuitun City falls within the VOC-sensitive regime during summer months, where O formation is primarily limited by VOCs availability. During winter, the regime shifts toward NO-sensitivity due to reduced photochemical activity.

The EKMA curves for January and July 2013 demonstrate this transition clearly. In January, the O isopleths show a strong dependence on NO concentrations, while in July, O formation becomes more sensitive to VOCs concentrations.

[Figure 10: see original paper]

[Figure 11: see original paper]

4 Conclusions

(1) O pollution was severe in Kuitun City during 2013–2015, with 10–33 days exceeding standards annually and maximum daily concentrations ranging from 0.385 to 0.457 mg · m^{3}.

(2) The diurnal variation of O showed a "U-shaped" curve, with peak concentrations occurring between 15:00–18:00 (around 17:00). The highest values appeared in summer, approximately 2.5 times greater than winter levels.

(3) VOCs concentrations exhibited seasonal variation, with summer values about 3 times higher than winter. In summer 2013, the average VOCs concentration reached 459 ppbv, with maximum hourly values up to 976 ppbv. Winter concentrations ranged from 13–60 ppbv.

(4) The relationships among O, VOCs, and NO showed distinct seasonal patterns. In summer, O formation was VOC-sensitive, while in winter it was NO-sensitive. The EKMA analysis confirmed that Kuitun City operates in a transitional regime, with control strategies needing seasonal adjustment.

(5) The photochemical smog pollution in Kuitun is controlled alternately by VOCs and NO, requiring targeted emission control strategies based on seasonal photochemical regimes.

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Abstract: This paper analyzes the relationships among O , VOCs, and NO concentrations over Kuitun City, Xinjiang, northwest China during 2013-2015 using environmental monitoring data. Results showed an apparent overload of O concentration over Kuitun City. O concentration was overloaded for 33, 14, and 10 days during 2013-2015, with daily maximum concentrations of 0.457, 0.396, and 0.385 mg · m ^{3}, respectively. Heavy O pollution occurred in summer, with values 2.5 times higher than in winter. The diurnal variation curve of O pollution was reversely "U-shaped" , with peak values occurring around 17:00. VOCs concentration in summer was 3 times higher than in winter, with no significant diurnal variation. High VOCs concentration and low O concentration occurred in winter. In summer, VOCs concentration changed with NO accordingly, and O concentration was the highest. This study indicated that O pollution occurred mainly in the sensitive areas of VOCs and NO , and was controlled alternatively by VOCs and NO .

Keywords: atmospheric environment; VOCs; O ; NO ; Kuitun; Xinjiang

Note: Figure translations are in progress. See original paper for figures.

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