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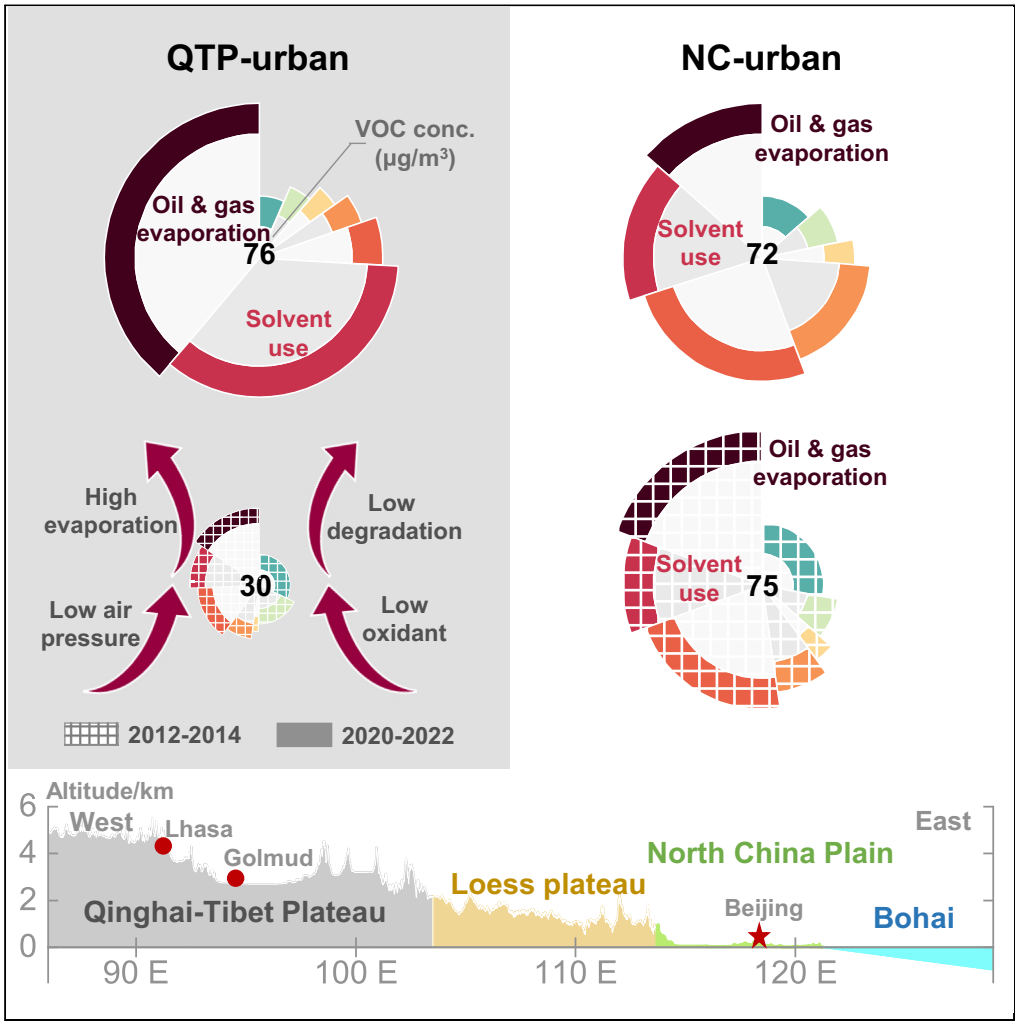

Guiqian Tang, Dan Yao, Yanyu Kang, ..., Xin Li, Jianchun Bian, Yuesi Wang

bjc@mail.iap.ac.cn (J.B.)
wys@mail.iap.ac.cn (Y.W.)

Highlights

VOCs concentration increases rapidly over the Qinghai-Tibet Plateau

Evaporation of oil and gas and solvent use are the main reasons for the VOCs increase

Slow degradation of VOCs is the secondary cause of the VOCs increase

VOCs emissions over plateau areas need to be controlled urgently

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The urgent need to control volatile organic compound pollution over the Qinghai-Tibet Plateau

Guiqian Tang,[1,8,9] Dan Yao,[3] Yanyu Kang,[1,4] Yuting Liu,[1,9] Yusi Liu,[5] Yinghong Wang,[1] Zhixuan Bai,[2] Jie Sun,[1] Zhiyuan Cong,[6] Jinyuan Xin,[1] Zhaoyun Liu,[1] Zhenyu Zhu,[1] Yejun Geng,[7] Lili Wang,[1] Tingting Li,[1] Xin Li,[1] Jianchun Bian,[2,9,*] and Yuesi Wang[1,9,10,*]

SUMMARY

Owing to the impact of the western development of China, there have been signs of air pollution over the Qinghai-Tibet Plateau in recent years. However, monitoring data on atmospheric volatile organic compounds (VOCs) are lacking in plateau areas. Here, VOCs concentrations in urban and background areas in North China and the Qinghai-Tibet Plateau were observed from 2012 to 2014 and 2020 to 2022, respectively. Compared to 2012–2014, the concentration of VOCs increased to 2.5 times in urban areas on the Qinghai-Tibet Plateau, which was equivalent to that in North China. Oil, gas, and solvent evaporation caused by a low atmospheric pressure is the primary factor for the increase in VOCs in plateau areas, and weak VOCs degradation is the secondary factor. Hence, we put forward the VOCs control strategies in plateau areas and point out the defects in the current research.

INTRODUCTION

Volatile organic compounds (VOCs) refer to all carbon-containing gaseous compounds except carbon monoxide and carbon dioxide.[1] These substances produce an uncomfortable smell, toxicity, irritation, teratogenicity, and carcinogenicity, which are harmful to human health.[2] In addition, VOCs are important precursors of ozone and secondary particulate matter, which exert a notable impact on photochemical and particulate matter pollution.[1]

There are two main sources of VOCs: biogenic and anthropogenic sources. Emissions of biogenic sources mainly originate from plants, while emissions of anthropogenic sources mainly originate from fuel combustion and solvent use.[1] With the implementation of the Action Plan for the Prevention and Control of Air Pollution from 2013, VOCs emitted during fuel combustion in China gradually decreased, while VOCs emitted due to solvent usage gradually increased.[3] At present, solvent use, industrial processes, and vehicle-related emissions are the main sources of VOCs in China.

In regard to the prevention and control of VOCs pollution, a large number of observations and studies have been conducted in China, and the temporal variation, spatial distribution, and chemical composition of VOCs have been clarified in recent years. These results indicate that the concentration of VOCs in China is significantly higher than that in developed countries in Europe and the United States.[4,5] Because VOCs emissions are closely related to the level of economic development, their spatial differences are significant in China.[6] The concentration of VOCs in urban areas is significantly higher than that in rural and background areas, and that in eastern China is significantly higher than that in western China.[7]

In 2000, China proposed a western development strategy. Since the implementation of western development for more than 20 years, the economy of the Qinghai-Tibet Plateau (Qinghai and Tibet) has rapidly developed. Compared to 2000, the number of civilian vehicles in the Qinghai-Tibet Plateau has increased by 14.4 times, the road freight volume has increased by 3.6 times, and the power consumption has increased by 7.6 times in 2020.[8] The increase in human activities has led to air pollution in plateau areas. Unfortunately, most of the observations and studies on VOCs are concentrated in Beijing-Tianjin-Hebei,

[1]State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China

[2]Key Laboratory of Middle Atmosphere and Global Environment Observation, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China

[3]School of Environment, Key Laboratory for Yellow River and Huai River Water Environment and Pollution Control, Ministry of Education, Henan Normal University, Xinxiang 453007, China

[4]Institutes of Physical Science and Information Technology, Anhui University, Hefei 230601, China

[5]State Key Laboratory of Severe Weather and Key Laboratory for Atmospheric Chemistry of China Meteorology Administration, Chinese Academy of Meteorological Sciences, Beijing 100081, China

[6]Institute of Tibetan Plateau Research, Chinese Academy of Sciences, Beijing 100101, China

[7]China Petroleum Engineering and Construction Corp. Beijing Design Branch, Beijing 100086, China

[8]State Environmental Protection Key Laboratory of Sources and Control of Air Pollution Complex, Beijing 100084, China

[9]University of Chinese Academy of Sciences, Beijing 100049, China

[10]Lead contact

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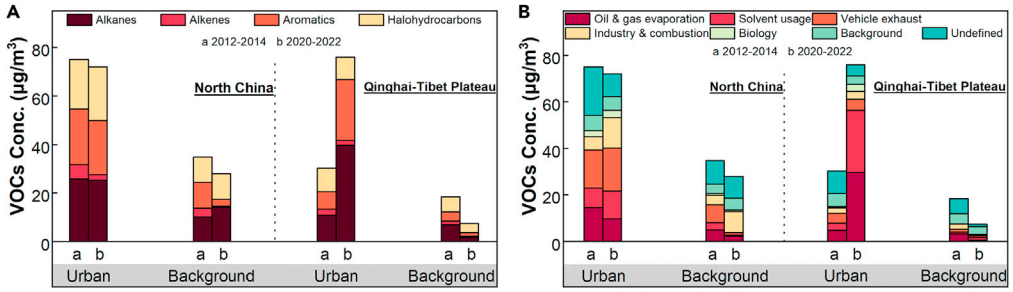

Figure 1. Chemical compositions and source contributions of VOCs

VOCs and its chemical compositions (A) and source contributions of VOCs (B) in North China and the Qinghai-Tibet Plateau from 2012 to 2014 and 2020–2022.

the Yangtze River Delta, and the Pearl River Delta, and observations on the Qinghai-Tibet Plateau are extremely rare.[9,10]

North China is the most polluted region in China, while the Qinghai-Tibet Plateau is the cleanest region in China.[11] To clarify the impact of economic development on VOCs pollution on the Qinghai-Tibet Plateau, this study collected VOCs observations in North China and the Qinghai-Tibet Plateau from 2012 to 2014 and 2020–2022, respectively. By comparing the observation results between these two periods, this paper attempted to reveal the trend of VOCs in the atmosphere above the plateau in recent years, clarify the main reasons for the evolution of VOCs pollution, and provide basic support for the prevention and control of air pollution on the Qinghai-Tibet Plateau.

RESULTS

VOCs concentrations

According to the urbanization level and pollution degree, the observation stations are divided into four types: urban and background stations in North China and urban and background stations on the Qinghai-Tibet Plateau. From 2012 to 2014, the VOCs concentrations in the urban and background areas in North China reached 75.1 and 34.8 μg/m^3, respectively, while the VOCs concentrations in the urban and background areas on the Qinghai-Tibet Plateau were 30.2 and 18.3 μg/m^3, respectively, which is consistent with observation results during the same period.[10,12] The concentration of VOCs on the Qinghai-Tibet Plateau was much lower than that in North China, with 40.2% and 52.6% in the urban and background areas of those in North China, respectively. Even the VOCs concentration in the urban areas on the Qinghai-Tibet Plateau was 13.4% lower than that in the background areas in North China (Figure 1A).

From 2020 to 2022, the VOCs concentrations in the urban and background areas in North China were 72.0 and 27.9 μg/m^3, respectively. Compared to 2012–2014, the concentration of VOCs in the urban and background areas decreased by 4.1% and 19.8%, respectively. Among all the species, halogenated hydrocarbons and alkanes remained constant as before, but the concentrations of alkenes and aromatics decreased significantly. These results are consistent with long-term observation results for Beijing.[13] On the Qinghai-Tibet Plateau, the VOCs concentration in the background areas also exhibited a downward trend, and the average VOCs concentration was only 7.3 μg/m^3. However, the trend in the urban areas of the Qinghai-Tibet Plateau differed from that in the other regions. Compared to 2012–2014, the concentration of VOCs in the urban areas on the Qinghai-Tibet Plateau increased to 76.0 μg/m^3, approximately 2.5 times higher than that from 2012 to 2014. From the perspective of the VOCs composition, halogenated hydrocarbons and alkenes remained constant as before, but alkanes and aromatics increased significantly, namely, by two times, over those from 2012 to 2014 (Figure 1A).

In summary, the ebb and flow in VOCs in these two regions have resulted in the fact that the concentration of VOCs in the urban areas on the Qinghai-Tibet Plateau is equivalent to that in North China. From 2012 to 2014, the concentration of all species in the urban areas on the Qinghai-Tibet Plateau was lower than that in North China, accounting for 31.3%–47.5% of all species in North China. Up to 2020–2022, halogenated hydrocarbons in the urban areas of the Qinghai-Tibet Plateau still accounted for approximately 40% of those in North China. However, alkanes and aromatics increased significantly, which were 1.6 and 1.1 times

*Correspondence:
bjc@mail.iap.ac.cn (J.B.),
wys@mail.iap.ac.cn (Y.W.)

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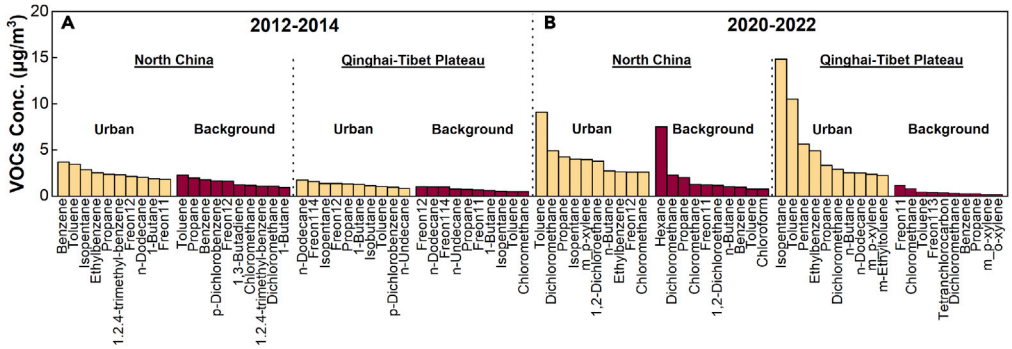

Figure 2. Ranking of the top ten dominant species of VOCs

Ranking of the top ten dominant species of VOCs in North China and the Qinghai-Tibet Plateau from 2012 to 2014 (A) and 2020–2022 (B).

those of North China, respectively. These two substances became the main species contributing to the increase in VOCs on the Qinghai-Tibet Plateau (Figure 1A).

VOCs markers

To identify the source of VOCs, the dominant species of VOCs in the different regions were analyzed. From 2012 to 2014, benzene, toluene, isopentane, and ethylbenzene were the main species in the urban areas of North China, which indicates that motor vehicles, industrial processes, and solvent usage were the main sources of VOCs. In the background areas of North China, VOCs were dominated by toluene, propane, benzene, freon 12, and methyl chloride, indicating that regional transport was another source of VOCs in addition to fuel combustion. During the same period, freon 114, isopentane, freon 12, propane, and n-butane and freon 12, freon 114, and freon 11 were the main species in the urban and background areas, respectively, of the Qinghai-Tibet Plateau, which indicates that long-range transport was the main source of VOCs on the Qinghai-Tibet Plateau (Figure 2).

From 2020 to 2022, the dominant species in the urban and background areas in North China changed insignificantly. Motor vehicles, industrial processes, and solvent use dominated VOCs emissions in the urban areas, while regional transport dominated VOCs emissions in the background areas. However, the proportions of isopentane, n-pentane, toluene, and ethylbenzene in the urban areas on the Qinghai-Tibet Plateau rose sharply, and the concentrations of these four species were 10.7, 10.7, 9.9, and 10.0 times those in 2012–2014, respectively (Figure 2). Previous studies have shown that the main VOCs due to gasoline exhaust and evaporation include isopentane, toluene, and n-pentane (Figure S1),[14] and the main components originating from solvent usage are toluene and xylene.[13] Therefore, the increase in these species indicates that the main source of VOCs in urban areas within plateau areas may be the heavy use of oil, gas, and solvents.

Source contribution

To quantify the contribution of emission sources to VOCs in the different regions, the positive matrix factorization (PMF) model was used from 2012 to 2014 and 2020–2022. A total of 6 types of emission sources were identified, including oil and gas evaporation, solvent usage, vehicle exhaust, industry & combustion, biogenic sources, and background sources. The source profiles of the different types of emissions are shown in Figure 3.

From 2012 to 2014, the main sources of VOCs in the urban areas in North China were vehicle exhaust, oil and gas evaporation, solvent usage, background sources, and industry & combustion, with contributions of 16.3, 14.5, 8.5, 6.4, and 5.8 $\mu g/m^3$, respectively (Figure 1B). The main sources of VOCs in the background areas in North China were similar to those at the urban stations, but the emissions of vehicle exhaust, oil and gas evaporation, and solvent usage were significantly lower than those at the urban stations, and their contributions reached only 30%–50% of those at the urban stations. The main emission sources were significantly different between the Qinghai-Tibet Plateau and North China, with contributions of 5.5, 4.7, 3.1, and 2.3 $\mu g/m^3$ from background sources, oil and gas evaporation, solvent usage, and industry & combustion, respectively. In addition, the main source in the background area of the Qinghai-Tibet Plateau was background sources, with a contribution of up to 4.4 $\mu g/m^3$.

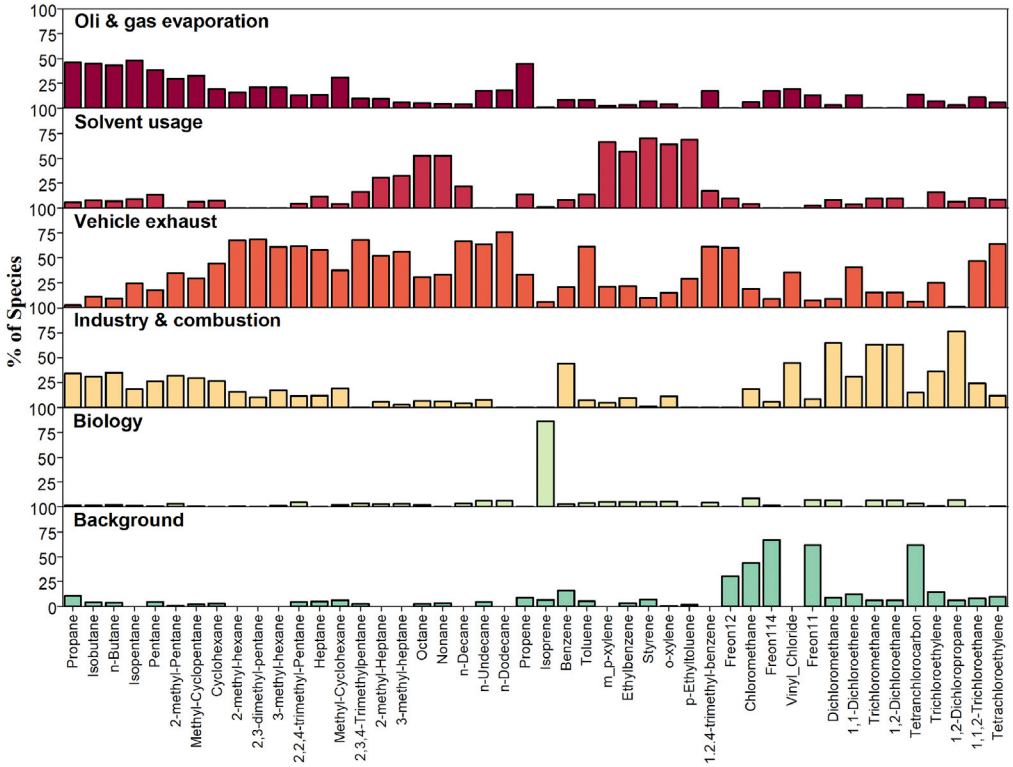

Figure 3. Source profiles of different emissions from the PMF model

Compared to 2012–2014, the source contributions of VOCs in the urban and background areas of North China and background areas on the Qinghai-Tibet Plateau changed insignificantly in 2020 and 2022, but the main emission sources of VOCs in the urban areas on the Qinghai-Tibet Plateau were significantly different. Compared to 2012–2014, although the main sources of VOCs for urban areas on the Qinghai-Tibet Plateau were still oil and gas evaporation, solvent usage, background contribution, and industry & combustion, the contributions of oil and gas evaporation and solvent usage increased significantly to 29.6 and 26.7 $\mu g/m^3$, respectively, which are 6.3 and 8.7 times previous levels. This result also confirms the previous speculation that oil and gas evaporation and solvent usage are the main contributors to the increase in VOCs in the urban areas of the Qinghai-Tibet Plateau.

DISCUSSION

Driving force of VOCs

The evaporation of oil and gas mainly comes from the evaporation of gasoline, diesel, and liquefied gas. In terms of gasoline, diesel, and liquefied gas consumption, the use of oil and gas products in the Qinghai-Tibet Plateau has increased from 2.1 in 2012 to 4.0 Mt in 2020,[8,15] which indicates an increase in oil and gas evaporation. The use of solvents mainly comes from architectural coatings, automobile repair, dry cleaning, mimeograph, etc. Industries such as dry cleaning and mimeograph printing are extremely underdeveloped on the Qinghai-Tibet Plateau, so their impact can be ignored. Automobile repair is related to the number of motor vehicles, and the use of architectural coatings is related to the construction of houses. Owing to the lack of data on solvent use in Qinghai and Tibet, the use of solvents is measured by the number of motor vehicles and the construction area of housing. From 2012 to 2020, the number of civilian vehicles in the Qinghai-Tibet Plateau increased from 71.9 million to 190.6 million, 2.7 times that of 2012.[8] Meanwhile, the housing construction area increased from 9.7 million m^2 to 14.0 million m^2, 1.4 times that of 2012.[8] Therefore, the number of civil vehicles and construction area represent the increase in solvent use over the Qinghai-Tibet Plateau.

Although the oil and gas consumption and solvent usage in plateau areas have increased in recent years, the activity intensity is far lower than that in eastern plain areas. How can a low human activity level cause a high level of VOCs pollution? The main reason for this phenomenon lies in the unique atmospheric

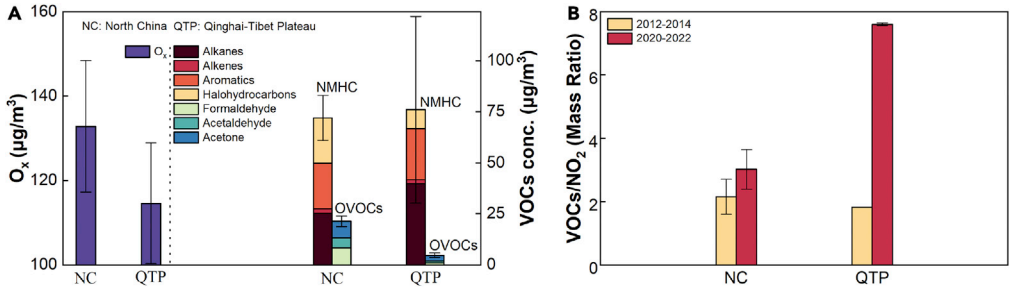

Figure 4. Ox, NMHC, OVOCs concentrations and VOCs/NO_2 ratios

Ox, NMHC, and OVOCs concentrations from 2020 to 2022 (A) and VOCs/NO_2 ratios from 2012 to 2014 and 2020–2022 (B) in North China and the Qinghai-Tibet Plateau.

environment of the Qinghai-Tibet Plateau. Compared to the plain area, the plateau air is thin, and the atmospheric pressure in Lhasa is only two-thirds of that in the plain area. As the atmospheric pressure decreases, the boiling point of VOCs decreases rapidly, resulting in faster evaporation of VOCs with a low boiling point. Choosing isopentane and toluene, the main components of oil and gas evaporation and solvent usage, as examples, the boiling points of isopentane and toluene are 301.0 and 383.7 K, respectively, under standard atmospheric pressure. However, in Lhasa, the boiling points of isopentane and toluene rapidly drop to 291.2 and 369.0 K, respectively, resulting in rapid evaporation of these substances into the atmosphere. Therefore, the evaporation of oil, gas, and solvent caused by a plateau low-pressure environment is the main cause of the increase in VOCs in recent years.

In addition to the emission of VOCs, the concentration level is also affected by the conversion rate of VOCs. The conversion of VOCs mainly occurs through reactions with ozone and its related species, and the main conversion products are oxygenated volatile organic compounds (OVOCs). Previous studies have shown that the concentration of total oxidant (Ox = nitrogen dioxide + ozone) can well characterize the atmospheric oxidation capacity.[16] By analyzing the Ox concentration (the average of daily maximum) over the Qinghai-Tibet Plateau and North China in 2020, the Ox concentration over the Qinghai-Tibet Plateau was 114.6 $\mu g/m^3$, which was significantly lower than the concentration over North China (132.8 $\mu g/m^3$) (Figure 4A). This result shows that the degradation capacity of VOCs in the Qinghai-Tibet Plateau is lower than that in North China. The OVOCs monitoring results also confirmed this conjecture. The concentrations of formaldehyde, acetaldehyde, and acetone in urban areas of North China were 8.3, 5.0, and 8.1 $\mu g/m^3$, respectively, in 2020. However, the concentrations of these pollutants in urban areas of the Qinghai-Tibet Plateau are only 1.0, 0.8, and 2.8 $\mu g/m^3$, respectively (Figure 4A). Considering that acetone mainly comes from primary emission and long-distance transportation, formaldehyde and acetaldehyde are used as the local conversion products. Therefore, the ratio of OVOCs (formaldehyde and acetaldehyde) to nonmethane hydrocarbon (NMHC) can be used as an indicator to measure the degradation capacity of VOCs in different regions. The OVOCs/NMHC ratio in urban areas of North China is 0.185, while that in urban areas of the Qinghai-Tibet Plateau is only 0.025. In conclusion, the longer lifetime of VOCs due to weak degradation is another important reason for the increase in their concentration over the Qinghai-Tibet Plateau.

Control strategies

The evaporation of oil, gas, and solvents is the main reason for the deterioration of VOCs pollution in the urban areas of the Qinghai-Tibet Plateau. To curb VOCs pollution on the Qinghai-Tibet Plateau, the following prevention and control suggestions are proposed.

Formulate local standards for plateau areas

In view of the unique plateau atmospheric environment, local vehicle oil and solvent standards should be examined and formulated. The aim is to improve the formulas of vehicle fuels and solvents, decrease the evaporation capacity of oil, gas, and solvents, and finally reduce the emission of toxic and harmful substances.

Structural reform of motor vehicles

With the implementation of the national VI standard, the full installation of carbon canisters will greatly reduce the evaporation of gasoline.[17] Therefore, the elimination of old motor vehicles is the primary means

to control VOCs emissions in plateau areas. In addition, the average boiling point of gasoline is 303–493 K and that of diesel is 453–643 K, and diesel is more difficult to volatilize. To reduce the emission of oil and gas evaporation, the feasibility of popularizing diesel vehicles in plateau areas should be demonstrated. Undoubtedly, the promotion of new-energy vehicles is also an effective means because these vehicles do not consume oil or gas.

Optimization of the industrial structure in the plateau region

Due to the fragile ecology of plateau areas, it is necessary to implement an industrial policy of combining the list of negative factors with the catalog of encouraged industries, dynamically adjust the catalog of encouraged industries in plateau areas, strictly restrict the development of highly volatile and toxic industries, and comprehensively prevent the spread of VOCs pollution.

Perspectives

Through the above analysis, VOCs pollution in the urban areas of the Qinghai-Tibet Plateau has deteriorated, which is significantly different from conventional cognition. This also indicates that there are still many loopholes in our current research.

Underestimation of emissions on the Qinghai-Tibet Plateau

Most of the current emission inventories of VOCs are calculated by multiplying emission factors and activity levels.[3] Because the impact of environmental conditions at different altitudes on emission factors is not fully considered, VOCs emissions in mountainous areas are seriously underestimated, inducing inconsistencies between simulations and observations.[18] At this stage, it is urgent to improve the VOCs emission inventory according to the environmental characteristics at different altitudes.

More importantly, the inconsistency between emission inventories and actual observations occurs not only in VOCs but also in other species. For example, with increasing altitude, the particle number concentration increases significantly, and the discharged particles change into fine-grained particles.[19–22] What is more surprising is that different altitudes can change not only the total amount of emissions but also the chemical composition of emissions. For example, with increasing altitude, the incomplete combustion of fuel will change the emission ratio of organic carbon and elemental carbon, and the content of water-soluble ions in particulate matter will decrease. Moreover, the emission source profiles of VOCs will change, and more isopentane will be detected in the substances emitted during coal combustion.[23] The change in total emissions and emission source profiles will greatly interfere with the subsequent source apportionment of air pollutants.

Amplified role of NOx on ozone pollution over the Qinghai-Tibet Plateau

Although the unique atmospheric environment above the Qinghai-Tibet Plateau causes a large amount of evaporation of VOCs, this exerts no significant impact on nitrogen oxide (NOx) emissions.[24] Therefore, the ratio of VOCs to NOx should increase significantly with increasing altitude. Statistical analysis shows that the ratio of VOCs and nitrogen dioxide (NO_2) on the Qinghai-Tibet Plateau and North China from 2012 to 2014 is approximately 2, with no significant spatial difference (Figure 4B). From 2020 to 2022, this phenomenon changes dramatically. With increasing altitude, the mass ratio of VOCs/NO_2 increases from 3.0 in plain areas to 7.6 in plateau areas (Figure 4B). As the ratio of VOCs to NOx is the most important indicator to identify ozone sensitivity to NOx and VOCs, this emission characteristic with increasing altitude will lead to changes in ozone sensitivity between the different altitudes. Notably, the plain area is more inclined to VOCs control, while the plateau area is more inclined to NOx control. In the future, the impact of the atmospheric environment on the emission of ozone precursors should be considered in the formulation of ozone control strategies on the Qinghai-Tibet Plateau.

Limitations of the study

Due to the harsh ecological environment of the Qinghai-Tibet Plateau, it is extremely difficult to sample for a long time on a large scale, which may lead to some limitations in the conclusions of this paper.

Spatial representation

From 2012 to 2014, only one urban station on the Qinghai-Tibet Plateau was observed. From 2020 to 2022, the number of urban observation stations increased to 2. A few sites may induce the problem of insufficient

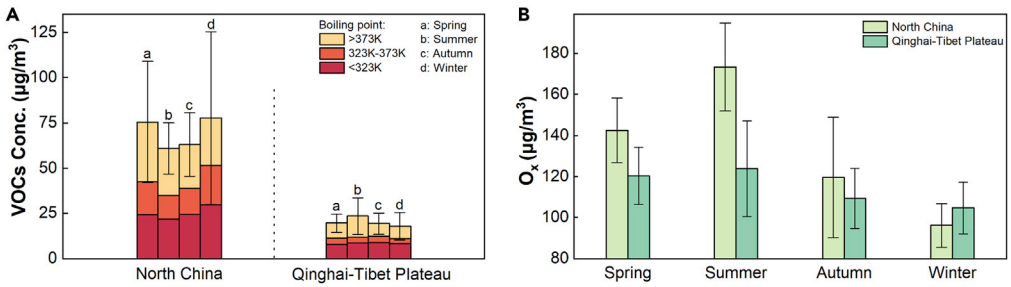

Figure 5. Seasonal variations in VOCs and Ox concentrations

Seasonal variations in VOCs at different boiling points during 2012-2014 (A) and Ox concentrations in 2020 (B) in North China and the Qinghai-Tibet Plateau.

representativeness of conclusions. However, due to the sparsely populated Qinghai-Tibet Plateau, the population was concentrated in only a few large cities. Lhasa and Golmud were the first and second largest cities in Tibet and Qinghai, respectively. Vehicle ownership in Lhasa accounted for 44% of Tibet, while Golmud was an important tourist transit place in Qinghai. Considering that the two stations are representative of urban areas on the Qinghai-Tibet Plateau, the existing conclusion may not be changed by adding more observation stations.

Temporal representation

Different VOCs have different volatilities. In principle, highly volatile substances should be more abundant in summer due to the high temperature. To illustrate this phenomenon, we analyzed the seasonal characteristics of VOCs using the observed data from 2012 to 2014 (Figure 5A). Surprisingly, the composition of VOCs in the Qinghai-Tibet Plateau and North China in different seasons did not change significantly due to the difference in volatility. Therefore, since a month-long sampling was conducted at each site during 2020–2022, the results can well reflect the average level of VOCs in different seasons.

However, the conclusion that VOCs degrade slowly still has limitations. The degradation of VOCs mainly occurs through the oxidation reaction with hydroxyl radicals, and the main product is OVOCs. Owing to the lack of hydroxyl concentration observations, the Ox concentrations are used to characterize the atmospheric oxidation capacity. The observation shows that the atmospheric oxidation capacity in the Qinghai-Tibet Plateau is weak and the concentration of oxidation products is low, which indicates that the degradation of VOCs in the Qinghai-Tibet Plateau is slow. However, if the study is carried out seasonally, we find that the concentration of Ox in the Qinghai-Tibet Plateau is higher than that in North China in winter (Figure 5B). Because the observation of OVOCs is only carried out in summer, it is urgent to carry out simultaneous observation of NMHC and OVOCs in winter to confirm the above conclusions.

In addition to the slow degradation of VOCs, there may be another reason for the low concentration of OVOCs. OVOCs are different from NMHC. The conversion of NMHC is mostly through the oxidation reaction with hydroxyl radicals, and the degradation of OVOCs also occurs through photolysis in addition to the above reaction. Owing to the high altitude and strong radiation in the Qinghai-Tibet Plateau, the photolysis rate of OVOCs in the plateau area should be significantly faster than that in the plain area, which may also be another reason for the low concentration of OVOCs.

Based on the above reasons, the increase in sampling stations and sampling periods will not change the conclusions of variations and the reasons for VOCs pollution in the Qinghai-Tibet Plateau. However, increasing the synchronous sampling of NMHC and OVOCs in different seasons may reveal the degradation and transformation mechanism of VOCs in the plateau area, which will play an important role in understanding the degradation pathway of VOCs in the plateau area in the future.

STAR★METHODS

Detailed methods are provided in the online version of this paper and include the following:

- KEY RESOURCES TABLE
- RESOURCE AVAILABILITY

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://doi.org/10.1016/j.isci.2022.105688.

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AUTHOR CONTRIBUTIONS

Conceptualization, G.Q.T.; Methodology, G.Q.T. and Y.S.W.; Formal Analysis, G.Q.T., D.Y., and Y.S.L.; Investigation, Y.Y.K., Y.T.L., Z.X.B., J.S., L.L.W., Z.Y.C., J.Y.X., Z.Y.L., and Z.Y.Z.; Resources, J.S. and Y.H.W.; Data Curation, G.Q.T.; Writing – Original Draft, G.Q.T.; Writing – Review & Editing, T.T.L., X.L., and J.C.B.; Visualization, Y.Y.K.; Supervision, G.Q.T., J.C.B., and Y.S.W.; Project Administration, J.C.B. and Y.S.W.; funding acquisition, J.C.B. and Y.S.W.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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STAR★METHODS

KEY RESOURCES TABLE

REAGENT or RESOURCE	SOURCE	IDENTIFIER
VOCs and NO_2 samples		
PAMS (57 species)	Spectra/Linde, UK	Catalog 1453600
TO-15 (65 species)	Spectra/Linde, UK	Catalog 1455236
CNEMC Mix (117 species)	Spectra/Linde, UK	Catalog 1532551
Internal standard (4 species)	Spectra/Linde, UK	Catalog 1514996
InertSep mini AERO DNPH 300 mg	GL Sciences Inc., JPN	SKU: 5010-23500
InertSep mini AERO Ozone Scrubber 1.5 g	GL Sciences Inc., JPN	SKU: 5010-23510
Acetonitrile	DiKMA technology Inc., CHN	CAS 75-05-8
DNPH Derivatives Standard (15 Species)	DiKMA technology Inc., CHN	Catalog 47230
NO 50 ppm N_2 Bal	Beijing AP BAIF Gases Industry Co., Ltd., CHN	CAS 10102-43-9
Deposited data		
NO_2	Ministry of Ecology and Environment of China	https://www.mee.gov.cn/
O_3	Ministry of Ecology and Environment of China	https://www.mee.gov.cn/
Civilian vehicles, road freight volume, power consumption	National Bureau of Statistics of China	http://www.stats.gov.cn/tjsj/ndsj/
Experimental model		
Positive Matrix Factorization Model	United States Environmental Protection Agency	https://19january2017snapshot.epa.gov/sites/production/files/2015-03/epa_pmf_5.0_setup.exe

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources, reagents and datasets should be directed to and will be fulfilled by the lead contact, Yuesi Wang (wys@mail.iap.ac.cn).

Materials availability

This study did not generate new unique materials.

Data and code availability

- All data reported in this paper will be shared by the lead contact upon request.
- The article does not report any new code.
- Any additional information required to reanalyze the data reported in this paper is available from the lead contact upon request.

METHOD DETAILS

Measurement sites

From 2012 to 2014, a total of 11 stations in North China and the Qinghai-Tibetan Plateau were sampled. There are six stations in North China and five stations in the Qinghai-Tibet Plateau. From 2020 to 2022, a total of 15 stations in North China and 4 stations in the Qinghai-Tibet Plateau were sampled. The station details, effective sample size and observation period can be found in the following tables.

Information of observations during 2012-2014

Site	Location	Category	Altitude	N	Time period
Beijing	North China	Urban	54 m	71	2012/1/3-2014/12/24
Xianghe		Urban	10 m	46	2012/3/20-2014/3/26
Yantai		Urban	32 m	109	2012/1/3-2014/11/19
Yucheng		Urban	22 m	99	2012/3/13-2014/12/24
Taiyuan		Urban	800 m	80	2012/3/13-2014/12/10
Xinglong		Background	940 m	137	2012/1/3-2014/12/31
Lhasa	Qinghai-Tibet Plateau	Urban	3617 m	80	2012/1/10-2014/11/26
Nyingchi		Background	3326 m	45	2012/4/10-2014/12/3
Ngari		Background	4264 m	53	2012/4/3-2014/2/5
Basong		Background	4300 m	75	2012/3/20-2014/11/5
Namtso		Background	4746 m	70	2012/1/3-2014/10/15

Information of observations during 2020-2022

Site	Location	Category	Altitude	N	Time period
Beijing	North China	Urban	54 m	136	2020/4/1-2020/8/14
Tianjin		Urban	10 m	136	2020/4/1-2020/8/14
Shijiazhuang		Urban	32 m	136	2020/4/1-2020/8/14
Baoding[a]		Urban	22 m	122/208[b]	2020/4/1-2020/7/31
Langfang[a]		Urban	13 m	122/129[b]	2020/4/1-2020/7/31
Xingtai[a]		Urban	72 m	122/212[b]	2020/4/1-2020/7/31
Tangshan[a]		Urban	45 m	122/211[b]	2020/4/1-2020/7/31
Zhengzhou		Urban	108 m	136	2020/4/1-2020/8/14
Anyang[a]		Urban	70 m	122/206[b]	2020/4/1-2020/7/31
Hebi[a]		Urban	40 m	122/212[b]	2020/4/1-2020/7/31
Jiaozuo[a]		Urban	102 m	122/212[b]	2020/4/1-2020/7/31
Xinxiang[a]		Urban	79 m	122/194[b]	2020/4/1-2020/7/31
Jinan		Urban	8 m	136	2020/4/1-2020/8/14
Taiyuan		Urban	800 m	136	2020/4/1-2020/8/14
Jincheng[a]		Urban	680 m	122/213[b]	2020/4/1-2020/7/31
Xinglong		Background	940 m	792	2020/9/11-2020/10/13
Lhasa[a]	Qinghai-Tibet Plateau	Urban	3617 m	45/56[b]	2020/8/8-2020/8/28
Golmud[a]		Urban	2800 m	64/89[b]	2021/8/3-2021/8/31
Basong		Background	4300 m	2	2022/5/6-2022/5/7
Qomolangma		Background	5200 m	18	2022/4/28-2022/5/6

[a]The stations marked with are those that conduct OVOCs sample collection synchronously.
[b]The numbers before and after the slash represent the sample size of NMHC and OVOCs respectively.

VOCs sampling

Summa canister (1 L, Entech Inc., USA) is used for NMHC sampling. The summa canister was cleaned three times (Entech 3100d, Entech Inc., USA) with nitrogen (99.995%) and finally vacuumized to 50 mTorr before sampling. During sample collection, an air pump (DOA-P504-BN, Gast, USA) is used to press the air into the summa canister and release it. After three repetitions, the air was pumped to 2.5 atmospheres[25].

A 2,4-dinitrophenylhydrazine (DNPH) cartridge (InertSep mini AERO-300 mg, GL Sciences Inc., Japan) was used to derive OVOCs. During sample collection, the DNPH was preceded by an ozone scrubber (InertSep

mini AERO Ozone Scrubber 1.5 g, GL Sciences Inc., Japan) and then connected to a pump in the back with a flow of 1 L/min for 3 hours. After sampling, the DNPH was sealed at both ends, wrapped in aluminum foil and stored in a refrigerator at 4 °C.[26]

VOCs analysis

Collected NMHC were detected via gas Chromatography - flame ionization detector/mass spectrometry (GC-FID/MS, Shimadzu QP2010SE/2020, Japan). First, the NMHC was concentrated in the enrichment traps (−165°C) after H_2O and CO_2 removal. Then, the condensed NMHC was volatilized at 150°C and were injected into the GC system with helium carrier gas. The initial temperature of the GC system was 35°C for 3 min, and then the GC oven was ramped at 6°C/min to 180°C, and held at 180°C for 5 min. Finally, 13 and 94 species were detected by FID and MS detectors, respectively, and quantified by internal (4 species, Spectra/Linde, UK) and external (117 species, Spectra/Linde, UK) standard methods together.[27] The precision, detection limit and correlation coefficients of the calibration curve of the selected species in this study can be found in Table S1 in the supplementary information.

The collected OVOCs were detected via high-performance liquid chromatography - ultraviolet (HPLC-UV) (UltiMate 3000, Thermo Fisher, USA). First, the DNPH sample was eluted with 5 mL acetonitrile, and then concentrated to 1.5 mL using a nitrogen blowing instrument. Then, 10 μL of the concentrated solution was injected into HPLC. After the OVOCs was separated by HPLC, 15 kinds of OVOCs were detected with 360 nm wavelength UV and quantified by an external standard method (DNPH Derivatives Standard, DiKMA Technology Inc., China).[28] Since formaldehyde, acetaldehyde and acetone accounted for more than 80% of all the species, these three substances were selected for analysis. The precision, detection limit and correlation coefficient of the standard curve of the three substances are shown in Table S2 in the supplementary information.

Source apportionment of VOCs

The Positive Matrix Factorization Model (EPA PMF V5.0 model, USEPA) was used to quantify the source contribution of VOCs in the different regions.[29] To ensure the stability of the PMF model, 46 species were selected for source apportionment, and the selected species accounted for greater than 80% of all species (Table S3). Then, 764 and 2446 samples were input into the model for 2012–2014 and 2020–2022, respectively (Table S4). With 6 factors, the modeled VOCs compared well to the measurement with a correlation greater than 0.99 (Figure S2), and the calculated results were stable enough because bootstrap was greater than 80% (Table S5). All the statistics of the base run indicated that the identified source profiles are reasonable in this study (Table S3). To ensure the preciseness of the results, species not involved in the PMF model are classified as undefined in addition to the other 6 factors.

Auxiliary data

To explain the ozone concentration and the ratio of VOCs to nitrogen dioxide (NO_2), the ozone and NO_2 data observed during the same period were used for auxiliary research. The NO_2 data of all stations from 2012–2014 and Golmud station in 2021 were obtained with a NOx analyzer (42i, Thermo Fisher, USA).[30] Ozone and NO_2 data in 2020 were obtained from the Ministry of Ecological Environment (https://www.mee.gov.cn/).