Emission of VOC Compounds from Ta-Shan Chemical Industrial Park in Middle China

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Abstract. VOCs emission from a Ta-Shan Chemical Industrial Park in January 1-8, 2014 and summer (July 16-20, 2014) have been studied in this paper. VOCs were collected by the stainless steel canisters and following pre-concentrate and analyzing by GC/MSD. The results showed that a total of 33 VOC species in winter samplers and 41 VOC species in summer samplers were detected. Among the 41 VOC species detected in the winter and summer samplers, 1-Butene and Ethane were the two most abundant compounds. Their highest average mean concentrations were 6013± 1758 and 3188± 1025 pptv in summer (contributed more than 12.5% and 4.8 % of the total VOC concentrations), and about 5895±1246 and 2763±789 pptv in winter (contributed more than12.9% and 7.8% of the total VOC concentrations), respectively. In winter, stack emission was found to be the main source of VOCs emission, while in summer, fugitive emission become the primary source.

1. Introduction
China has made great economic achievements these years. However, as the sharp increase costs of land utilization and labor, thousands of factories moving from coastal city to the middle and west China such as Jiangxi province, Hunan province, Anhui province, Hubei province and Sichuan province, some of them even moved out of China to Southeast Asia such as Vietnam, Thailand and Malaysia. The incoming factories not only bring the immeasurable economic benefits to the local government, but also bring a successive environment problem such as air quality deterioration. In 2013, the number of national average haze days is 4.7, 2.3 more than the long term average (2.4), and is the highest level since 1961[1]. In northern Jiangsu and central Henan, the haze days were more 10 days even 15 days more than the long term average1. What's worse, in 2014, a wide range of long time haze appeared for the first time in the Middle China and even worse in 2015 and 2016. The composite-regional air pollution has become the prominent environmental problem in China now.

Volatile organic compounds (VOCs) are defined as organic compounds that with high volatility and can easily participate in photochemical reactions [2]. It also play an prominent role in the formation of ozone and secondary organic aerosol (SOA), which two were considered to have strong correlation with the composite-regional air pollution [3,4].Recent studies have shown that chemical industries are a major source of volatile organic compounds in the urban city, like Guangzhou[5], Houston[6], and Hongkong[7]. Zheng et al. found that solvent use-related industrial sources account for more than 80% of the total VOC emission in the Pearl River Delta region in 2011[5]. Chen et al.
suggested that a chemical park was an odorous source that affected the population near the industrial district [8]. Therefore, investigating VOC emission characteristics in the chemistry industrial park is critical for understanding the formation of composite-regional air pollution and devising effective control policies.

2. VOCs Sampling and Analyzing
Ta-Shan chemical industrial park is located at east of Leping City (Longitude 116°53′36″ - 117°32′40″ E, latitude 28°42′14″ -29°23′24″ N), the southern suburbs, with the total planning area of 10 km² in the middle-east of Jiangxi province. And the park is one of the largest industrial park in middle-south China. The leading industry were fine chemistry and pharmaceutical chemistry. Leping has a humid subtropical climate with four distinct seasons. Winters are short and fairly mild (average low in January is 2°C or 35.6°F), but with occasional frosts and snow is not unheard of. Summer is long and humid, with amongst the highest temperatures in China (average 34°C or 93°F in July).

Stack emission and fugitive emission samples were collected from 3 selected plants in the Ta-Shan chemical industrial park in winter (January 1-8, 2014) and summer (July 16-20, 2014). The ambient air samplers were all carried out at the core of each selected plant. Manufacturing workshop, warehouses of raw materials and goods, stack emission also be selected for the sampling sites. VOCs samplers were collected by using a leak-free, two-liter, stainless steel canister (UCI, USA) equipped with a restricted sampler operating at 38 mL/min (Entech Instrument Inc., California, USA). VOCs were first preconcentrated in the preconcentrator then analyzed by GC-MSD or GC-FID/ECD. The Gas chromatogram of a standard mixture of 55 Non-methane hydrocarbons (NMHCs) showed in Figure 1. And all the VOC compounds showed the good correlation coefficient (R²>0.99).

![Gas chromatogram of a standard mixture of 55 Non-methane hydrocarbons (NMHCs)](image)

1. Isobutane, 2. 1-butene, 3. n-Butane, 4. trans-2-butene, 5. cis-2-Butene, 6. 3-methyl-1-butene, 7. Isopentane, 8. 1-pentene, 9. 2-methyl-1-butene, 10. n-pentane, 11. Isoprene, 12. cis-2-pentene, 13. 2-methyl-2-butene, 14. 2,2-dimethyl-butane, 15. cyclopentene, 16. 4-methyl-1-pentene, 17. cyclopentane, 18. 2-methylpentane, 19. 3-methylpentane, 20. 1-hexene, 21. n-hexane, 22. 2-hexene, 23. 3-hexene, 24. methylcyclopentane, 25. 2,4-dimethylpentane, 26. Benzene, 27. Cyclohexane, 28. 2-methyl-hexane, 29. 2,3-dimethyl-pentane, 30. 3-methyl-hexane, 31. 2,2,4-trimethyl-pentane, 32. n-heptane, 33. Methylcyclohexane, 34. Fluorobenzene (IS), 35. Toluene, 36. 2-methyl-heptane, 37. 3-methyl-heptane, 38. n-octane, 39. Chlorobenzene-d5 (IS), 40. Ethylbenzene, 41. m/p-Xylene, 42. Styrene, 43. o-Xylene, 44. n-nonane, 45. 4-bromo-fluorobenzene, 46. Isopropylbenzene, 47. α-Pinene, 48. n-propylbenzene, 49. p-ethyltoluene, 50. 1,3,5-trimethyl-benzene, 51. o-ethyltoluene, 52. 1,2,4-trimethylbenzene, 53. n-Decane, 54. 1,2,3-trimethylbenzene, 55. m-diethylbenzene, 56. p-diethylbenzene, 57. o-diethylbenzene

3. Results and Discussion
VOCs concentrations were measured by analyzing the averaging results of samples from different industrial sectors or processes, such as manufacturing workshop, warehouse of goods and raw
materials, stack emission and ambient levels. These sectors were divided into “fugitive emission”, “stack emission” and “ambient levels”. A total of 33 VOC species in winter samplers and 41 VOC species in summer samplers were detected in this study. Arithmetic mean concentrations of top 10 highest VOC compounds were listed in Table 1 along with the corresponding standard deviation (SD).

Among the 41 VOC species detected in the winter and summer samplers, 1-Butene and Ethane were the two most abundant compounds. Their highest average mean concentrations were 6013±1758 and 3188±1025 pptv in summer (contributed more than 12.5% and 4.8% of the total VOCs concentrations), and about 5895±1246 and 2763±789 pptv in winter (contributed more than 12.9% and 7.8% of the total VOC concentrations), respectively. It was easy to see from Table 1 that the total VOCs concentrations varied widely between the different industrial sectors or processes. Among the three types of sectors, stack emission showed the highest total VOC concentrations (45765 pptv) in winter. The descending order of total mean concentration was stack emission> fugitive emission> ambient levels and the ratio of the three was 43%: 34%: 23%. While in summer, fugitive emission increased sharply, which contributed more than 48% of the total VOC mean concentration compared to 35% of stack emission. This might be explained by that high temperature in summer might accelerate the speed of VOCs leaking from the Valves, Tank lids or Pumps. The results implied that fugitive emission might be one of the most important VOCs source in the chemical industrial park in summer and inside manufacturing workshop and warehouse were important microenvironment for exposure to VOCs, especially in summer. In consideration of gaining more economic benefit while avoiding healthy and environmental problems on the same time, some strategies must be adopted for controlling the VOCs Leaking.

4. Conclusions
The characteristic of VOCs emission from Ta-Shan Chemical Industrial Park have been discussed above. A total of 33 VOC species in winter samplers and 41 VOC species in summer samplers were detected. The highest total VOCs of 65757 pptv showed fugitive emission was the main source of VOCs in summer, while stack emission was main source in winter (45765 pptv). The manufacturing workshop and warehouse were important microenvironment for exposure to VOCs, especially in summer. It is now widely recognized that industry must decrease its environmental influence to allow the sustainable development and a major contributing factor will be through controlling emissions. This will be driven by a combination of public pressure, environmental legislation and enterprises' social responsibility.

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References
[1]  Government report 2013 China Meteorological Administration http://www.cma.gov.cn.
[2]  Kota S H and Park C.H 2014 Atmospheric Environment 82(1) 24-35.
[3]  Chen W H and Persily A K2014 Building and Environment 71(71)204-211.
[4]  Wei WJ and Xiong JY 2014 Atmospheric Environment 82(1) 327-334.
[5]  Zheng JY 2013 Science of TheTotal Environment 456(7) 127-136.
[6]  Zhao W and Hopke PK 2004 Environment Science and Technology 38(5) 1338-1347.
[7]  Zheng JY and Zhong L J 2010 Atmospheric Environment 44(6) 814-823.
[8]  Chen LY and Jeng FT 2000 Environment Science and Technology 34(7) 1166-1173.
Table 1 Mean±SD concentration (pptv) of top 10 highest VOC compounds in Ta-Shan chemical industrial park.

| VOC species          | Winter          |       |       | Summer          |       |       |
|----------------------|-----------------|-------|-------|-----------------|-------|-------|
|                      | F (n=10)        | Range| Mean  | A (n=5)         | Mean  | Range|
| 1-Butene             | 354±1236        | 2360-4586 | 5895±1246 | 3315-7951 | 1739±367 | 1871-3255 | 4348±1518 | 3850-5540 | 601±758 | 5215-6687 | 3300±369 | 2860-3382 |
| Ethane               | 276±789         | 1611-343 | 265±790 | 1514-2885 | 197±562 | 1298-2469 | 3188±1025 | 1491-3712 | 2568±588 | 2131-2619 | 2067±464 | 1712-2269 |
| Acetylene            | 155±552         | 1310-1798 | 178±658 | 1278-1985 | 131±325 | 978-1463 | 176±657 | 1256-2015 | 223±673 | 1847-2486 | 155±427 | 1457-1679 |
| Isobutane            | 141±338         | 989-1285 | 189±552 | 1668-1980 | 1284±368 | 987-1561 | 1207±485 | 1045-1453 | 250±568 | 1985-2760 | 134±368 | 1240-1586 |
| n-Hexane             | 126±257         | 887-1125 | 207±775 | 1587-2575 | 117±178 | 872-1220 | 1157±368 | 961-1256 | 211±589 | 1846-2368 | 101±162 | 875-1155 |
| Acetone              | 126±860         | 1283-2450 | 1887±661 | 1771-2103 | 1003±253 | 854-1278 | 295±882 | 2668-3360 | 261±610 | 2272-2987 | 92±158 | 860-1059 |
| Propene              | 178±545         | 1730-2211 | 155±768 | 1265-1930 | 74±312 | 411-821 | 1986±428 | 1769-2153 | 241±658 | 2014-2689 | 894±123 | 770-968 |
| Ethene               | 912±46          | 856-1126 | 1257±518 | 1032-1556 | 704±64 | 515-958 | 1156±321 | 1027-138 | 135±542 | 1158-1470 | 87±138 | 856-985 |
| Isopentane           | 1269±589        | 779-1332 | 156±654 | 1336-1882 | 743±361 | 257-1054 | 1387±582 | 975-1421 | 189±611 | 1535-2164 | 814±341 | 684-1089 |
| Methyene chlorde     | 1668±887        | 1258-1826 | 350±1442 | 2750-3995 | 777±218 | 478-895 | 1790±550 | 1680-1985 | 306±785 | 3116-3998 | 750±198 | 615-878 |
| Others               | 1727±65         | -     | 2189±65 | -     | 1178±65 | -     | 322±65 | -     | 212±65 | -     | 113±65 | -     |
| Total VOCs           | 35402           | 45764 | 24394 | 65757 | 4802 | 24880 | - | - | - | - | - | - |

a fugitive emission; b stack emission; c ambient level; d six samples average. 
<sup>e</sup> Total of 25 other VOC species detected in winter samples (including Propene, Dimethyl ether, n-Butane, n-Pentane, Butanal, 2-methyl propanal, Tetrahydro furan, 1,2-dichloroethane, Benzene, Cyclohexene, trimethyl-2-pentene, Toluene, Chlorobenzene, Ethylbenzene, m,p-Xylene, 5-methyl-3-hexanone, o-Xylene, Benzaldehyde, a-pinene, Octanal, tert-butyl-benzene, 4-methyl-benzaldehyde, Naphthalene).
<sup>f</sup> Total of 31 other VOC species detected in winter samples (Propene, Dimethyl ether, n-Butane, n-Pentane, Butanal, 2-methyl propanal, Tetrahydro furan, 1,2-dichloroethane, Benzene, Cyclohexene, trimethyl-2-pentene, Toluene, Chlorobenzene, Ethylbenzene, m,p-Xylene, 5-methyl-3-hexanone, o-Xylene, Benzaldehyde, a-pinene, Octanal, tert-butyl-benzene, 4-methyl-benzaldehyde, Naphthalene, n-Pentane, n-Octane, Ethyl-benzene, 2-Butanone, Styrene, Ethyl acetate, 3-methyl-hexane, 2,3-Dimethyl-pentane).