Case study of VOCs observation using Canister-GC/MS method in Japan

Kouki Sasaka
Leader of a research group on atmospheric environment
Center for Environmental Science in Saitama (Japan)

What are volatile organic compounds (VOCs)?

☆A general term for organic compounds that easily volatilize into the atmosphere at normal temperature and pressure.

☆A wide variety of compounds are classified as volatile organic compounds (VOCs; more than several hundred, including toluene, xylene, ethyl acetate, and benzene).

☆Widely used as solvents or cleaning agents for paints, adhesives, etc., taking advantage of their characteristics such as easy volatilization and lipophilic properties.

⇒ Emitted in various situations such as painting, construction work, printing, degreasing cleaning, and vehicle refueling.

1

Issues of VOCs in the atmospheric environment

☆Potential sources of odor complaints.

☆Even at low concentrations, long-term exposure may be hazardous to human health.

☆Potential sources of particulate pollutants and photochemical oxidants (Ox).

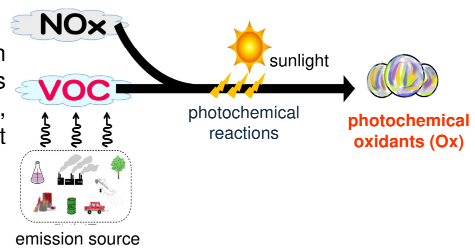
⇒ Various studies and monitoring are being conducted to contribute to the resolution of the two main issues listed below.

2

Ox and Photochemical smog

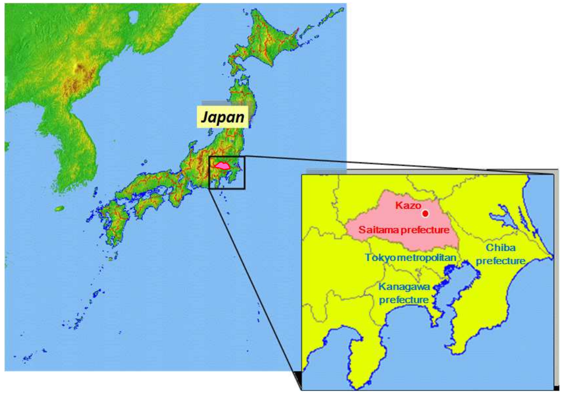
【Ox】
Causative substances of the phenomenon known as photochemical smog. In Japan, environmental standards have been established for Ox.

【Photochemical smog】
A phenomenon in which nitrogen oxides (NOx) and VOCs from vehicles and factories react with sunlight, producing Ox (mostly ozone) that create a hazy, white sky.



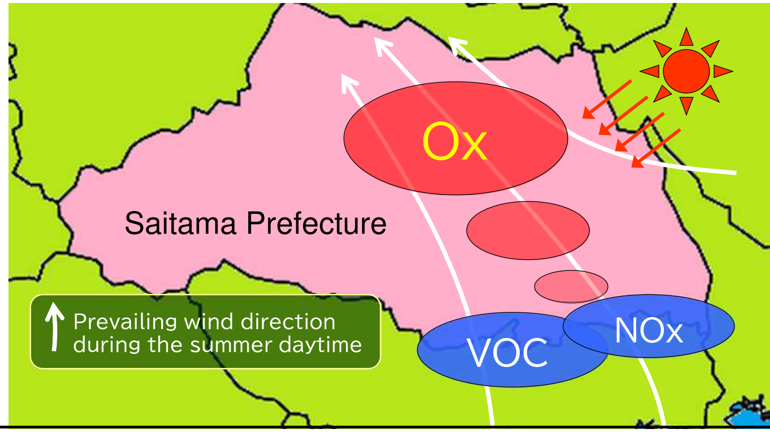
3

Saitama prefecture



4

Increasing in Ox concentrations during summer



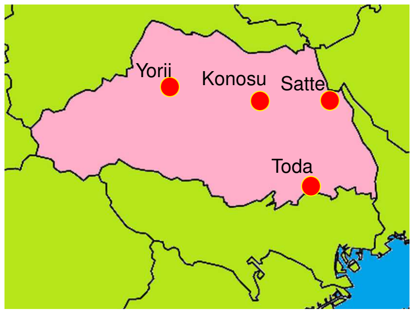
5

Observation of VOCs components that significantly contribute to Ox formation

☆Once per month during the warm season (May-September)

☆Four sites in Saitama Prefecture

☆Samples were taken during the daytime (6:00 am - 6:00 pm) and nighttime (6:00 pm - 6:00 am)



6

Sampling and analysis

☆Sampling

・**VOCs samples**：Canister sampling method

・**Aldehydes and ketones**：Solid phase trapping method

⇒ In both cases, timer sampling was conducted by day and night.

☆Analysis

・**Low bp. VOCs*** ：GC-FID method

*ethane, propane, ethylene, acetylene, and propylene

・**Other VOCs**：(Canister-)GC/MS method

・**Formaldehyde and acetaldehyde**：HPLC-DAD method

・**Other aldehydes and ketones**：LC/MS/MS method

7

Compounds analyzed in the survey (1)

☆Saturated hydrocarbons (alkanes)

- Ethane
- Propane
- Isobutane
- n-Butane
- Isopentane
- n-Pentane
- Cyclopentane
- 2,2-Dimethylbutane
- 2-Methylpentane
- 3-Methylpentane
- n-Hexane
- Methylcyclopentane
- Cyclohexane
- 2,4-Dimethylpentane
- 2-Methylhexane
- 2,3-Dimethylpentane
- 3-Methylhexane
- n-Heptane
- Methylcyclohexane
- 2,2,4-Trimethylpentane
- 2,3,4-Trimethylpentane
- 2-Methylheptane
- 3-Methylheptane
- n-Octane
- n-Nonane
- n-Decane
- n-Undecane

☆Unsaturated hydrocarbons (alkenes)

- Ethylene
- Acetylene
- Propylene
- trans-2-Butene
- cis-2-Butene
- 1,3-Butadiene
- 1-Pentene
- Isoprene
- trans-2-Pentene
- cis-2-Pentene

8

Compounds analyzed in the survey (2)

☆Aromatic hydrocarbons

- Benzene
- Toluene
- Ethylbenzene
- m-/p-/o-Xylene
- Styrene
- Isopropylbenzene
- n-Propylbenzene
- m-/p-/o-Ethyl toluene
- 1,2,3-Trimethylbenzene
- 1,2,4-Trimethylbenzene
- m-/p-Diethylbenzene

☆Halogenated compounds

- Chloromethane
- Dichloromethane
- Chloroform
- Carbon tetrachloride
- Bromomethane
- Chloroethane
- 1,1-Dichloroethane
- 1,2-Dichloroethane
- 1,1,1-Trichloroethane
- 1,1,2-Trichloroethane
- 1,2-Dibromoethane
- 1,1-Dichloroethylene
- cis-1,2-Dichloroethylene
- Trichloroethylene
- Tetrachloroethylene
- 1,2-Dichloropropane
- cis-1,3-Dichloropropane
- trans-1,3-Dichloropropane
- Chlorobenzene
- o-/m-/p-Dichlorobenzene

9

Compounds analyzed in the survey (3)

☆Freons

- CFC11
- CFC12
- CFC113
- CFC114
- HCFC22
- HCFC123
- HCFC141b
- HCFC142b
- HCFC225ca
- HCFC225cb
- HFC134a

☆Aldehydes

- Formaldehyde
- Acetaldehyde
- Propionaldehyde
- n-Butyraldehyde
- Isobutyraldehyde
- Valeraldehyde
- Benzaldehyde
- Hexanal

☆Ketones

- Acetone
- Methyl ethyl ketone
- Methyl isobutyl ketone

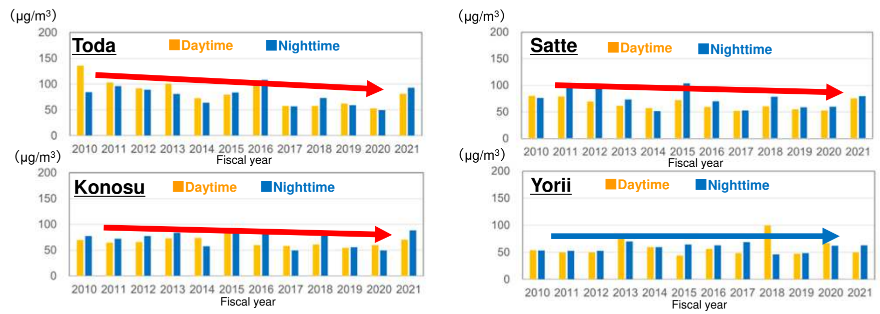
☆Others

- Acrylonitrile

A total of 97 compounds were analyzed.

10

Annual trends in the average total VOCs concentration of the compounds



11

Annual trends in the average total VOCs concentration of the compounds

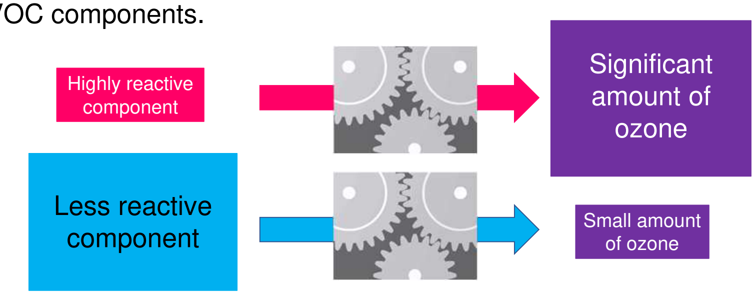
Urban areas (Toda, Kounosu, and Satte)
Total VOCs concentration has been decreasing.
⇒ This trend aligns with estimated VOC emissions, indicating the effects of emission reductions.

Suburban area (Yorii)
Total VOCs concentration has remained stable.
⇒ Due to the lack of nearby anthropogenic sources.

12

Maximum Incremental Reactivity (MIR)

Ozone formation potential varies depending on the specific VOC components.



MIR：Defined as the maximum amount of ozone that a unit quantity of each VOC component can produce in the atmosphere.

13

An example of MIR

trans-2-Butene: 13.28
cis-2-Butene: 13
1,3,5-Trimethylbenzene: 12.54
Toluene: 4.66
m-Xylene: 11.71
o-Xylene: 7.45
p-Xylene: 4.04
Ethyl cellosolve: 3.69
Butyl cellosolve: 2.34
Methyl ethyl ketone: 2.1
Cyclohexane: 1.42
n-Pentane: 1.4
Isobutane: 1.29
n-Butane: 1.25

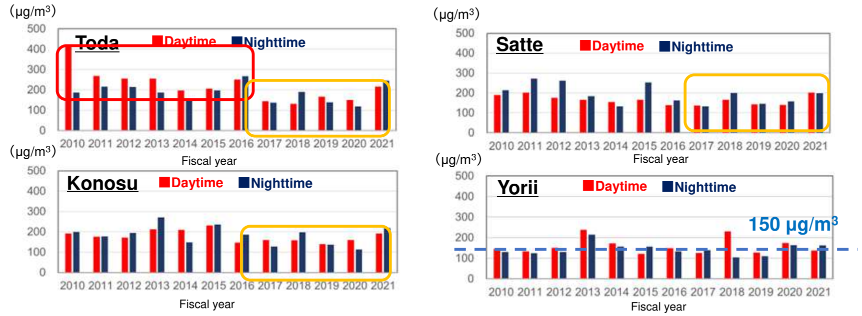
n-Hexane: 1.21
Methanol: 1.1
Ethyl Acetate: 0.6
Trichloroethylene: 0.59
Acetone: 0.5
Isopropyl Alcohol: 0.47
Decane: 0.46
Undecane: 0.32
Ethane: 0.3
Chloroethane: 0.25
tert-Butyl Acetate: 0.2
1,2-Dichloromethane:0.106
Dichloromethane: 0.07
Methyl Formate: 0.067

1,1,2-Trichloroethane: 0.064
Tetrachloroethylene: 0.046
Ethylene Oxide: 0.045
Chloroform: 0.038
Chloromethane: 0.036
Methane: 0.0146
HCFC-225ca: 0.0058
HFC-43-10mee: 0.004
HCFC-22: 0.0039
HCFC-142b: 0.0035
HCFC-141b: 0.0031
HCFC-225cb: 0.0029
HCFC-124: 0.0027

The ability to form ozone was evaluated by multiplying this MIR by the concentration of each VOC component.

14

Annual trend in ozone formation potential of VOCs



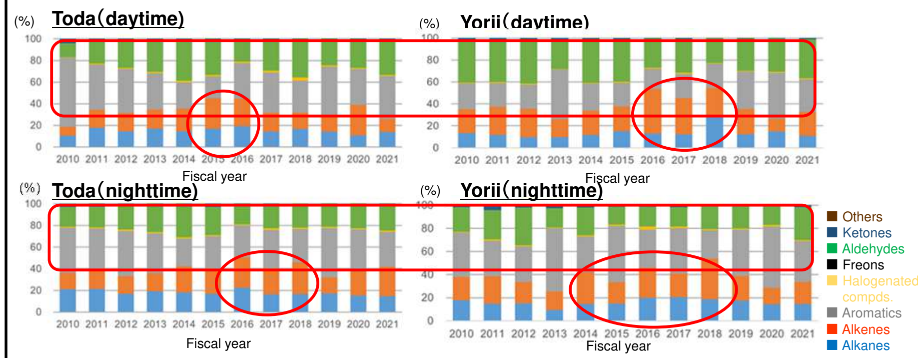
15

Annual trend in ozone formation potential of VOCs

- In Toda, daytime ozone formation potential above 200 μg/m^3 were common until 2016, but are now similar to Konosu and Satte, with more recent instances of higher nighttime levels.
- Yorii remains stable around 150 μg/m^3.
- Konosu and Satte have slightly higher potential than Yorii, with an increase in nighttime cases recently.

16

Annual trend in the proportion of VOC components in ozone formation potential



17

Annual trend in the proportion of VOC components in ozone formation potential

- In both cases, the contributions of aromatic hydrocarbons (shown in gray) and aldehydes (shown in green) are significant.
- There are also cases where the contributions of alkanes (shown in light blue) and alkenes (shown in orange) are comparable.

⇒ These results suggest the need for measures in future ozone management strategies.

18

Conclusion

☆Analyzed data from four locations in Saitama Prefecture (Toda, Kōnosu, Satte, Yorii) on ozone formation components.

- Urban areas (Toda, Konosu, and Satte) show decreasing VOC concentrations, likely due to emission reductions. On the other hand, in suburban area (Yorii) shows limited effects from fewer anthropogenic sources.
- The ozone formation potential is higher in urban areas than suburban area.
- Major contributors include aromatic hydrocarbons and aldehydes, with significant roles for alkanes and alkenes, indicating a need for countermeasures.

19