

CORRELATION OF THE RATIO OF NON-METHANE HYDROCARBON AND NITROGEN OXIDES CONCENTRATION IN THE ATMOSPHERE AND OUTDOOR ENVIRONMENT

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ABSTRACT

The correlation of atmospheric pollution by VOC and NMHC/NO_x ratio has been found. By using NMHC/NO_x ratio, the source of NMHC in the region can be presumed without effects from the diffusion and the dilution by the meteorological conditions. At general measurement station in A city Osaka Prefecture, the NMHC/NO_x ratio shows high value in summer though NMHC and NO_x concentration show high value in early winter. As opposed to city A, traffic measurement station C doesn't show this pattern. It suggests that the amount of the exhaust of NMHC increases along with the temperature. The waste plastic processing facility was able to become a non-combustion system source in city A. By comparing the transition annual NMHC/NO_x ratio at measurement station A and B, the waste plastic processing facility resulted to increase NMHC/NO_x ratio. Ventilation is not useful for the improvement of indoor air quality when outdoor pollution level is higher than indoors. Therefore, the NMHC/NO_x ratio can show the amount of the NMHC generation of non-combustion origin without receiving the influence of meteorological conditions. NMHC/NO_x ratio is a useful index to evaluate the change in the regional environment by the VOC s pollution. This ratio of outdoor air can be adapted to ventilation control.

KEYWORDS

Regional environment, Nitrogen oxide, Non-methane hydrocarbon, NMHC/NO_x ratio, VOC emission source

INTRODUCTION

Volatile Organic Carbons are not only harmful but also become the source of suspended particulate matter (SPM) and photochemical oxidant. Moreover, revised Air Pollution Control Law announced that VOC emission must be reduced more in 2004. However, it is necessary to report amount of VOC emission in large scale facilities such as painting, printing and VOC storage tanks but is self management in small scale facilities. Contents of emitted VOC are not only well-established materials used in industry activity but also unintentionally-generated materials such as dioxin. There isn't a easy and enough method to evaluate effect that is these unknown VOC gives the regional environment. Even if a small scale facility belching various VOC was built in a residential area, deterioration of the regional environment is unnoticed until the local residents' health problems are reported. On the other hand, measurement station (public station: 1639, traffic station: 447) is built and have measured SO₂, NO, NO₂, NO_x, CO, NMHC, in Japan. NMHC measured at measurement station is considered to be an index of VOC in the atmosphere by expressing various kinds of VOC by a ppm unit in terms of the density of methane containing one carbon element (methane is excluded from NMHC because it's low photochemical activity). In this study, measured NMHC is used as a standard of the VOC and Carbonyl compounds concentration in the atmosphere. The researches which evaluate change of regional environment using change of NMHC or NO_x concentration were not reported. The sources of NMHC are classified roughly into combustion of the fuel such as effluent gas of car or boiler

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(combustion origin) and non-combustion of the fuel such as painting facility or chemical plant (non-combustion origin). Combustion origins emit NMHC and NO_x, NMHC is mainly generated by incomplete combustion and NO_x is thermal NO_x which generated by combustion of the fuel. Non-combustion origins emit only NMHC. NMHC/NO_x ratio calculated with NMHC and NO_x becomes index which judges NMHC generation is combustion origin or non-combustion origin. The level of the air pollution in regional environment depends on the amount and the diffusion of the pollutants from the generation sources. In this study, the change of regional environment was evaluated by the change of NMHC/NO_x ratio without being affected from the diffusion and the dilution by the meteorological conditions. Additionally, the influence of outdoor air quality on indoor air quality was considered.

METHOD

The calculation method of the NMHC/NO_x ratio

NMHC/NO_x ratio was calculated by means of concentration of NMHC(ppmC) and NO_x(ppm) measured at the general measurement stations or the traffic measurement station. The monthly average value was used to review the seasonal change of the regional environment, and the yearly average value was used to review the influence of the construction of the fixed sources. Unit of NMHC/NO_x ratio used to evaluate is ppmC/ppm.

The NMHC/NO_x ratio at A,B and C stations

Osaka city A was chosen as an example of regional environment assessment, transition of NMHC/NO_x by construction of non-combustion origin was considered. In A city, there are the incineration facility, the waste plastic processing facility, etc. near the residential area. The second waste plastic processing facility and the construction of the highway are being planned, too. Public measurement station of city A is at 1Km point from this area, so that it is believed that the data measured at this station can express environment of this area. NMHC and NO_x discharged from fixed origin are diluted and spread similar. Additionally, public measurement station B (The distance between A and B is 12km) and traffic measurement station C (The distance between A and C is 3Km) near city A were chosen as the contrast stations, and each transition of NMHC/NO_x ratio of these stations was compared with NMHC/NO_x ratio of station A.

Measurement survey

The concentration of VOC and Carbonyl compounds were measured in the periphery of the waste plastic processing facility in A city. VOC was collected to ATD tube which filled up TenaxA and Carboxen by 100ml/min for 3hours. The ATD tubes after sampling were analyzed by TD-GC/MS. Carbonyl compounds were collected to DNPH cartridge by 1L/min for 3 hours. DNPH cartridges after sampling were analyzed by HPLC after solvent extraction by acetonitrile.

RESULT and DISCUSSION

Seasonal Change of NMHC value and NO_x value at A, B and C stations

Figure 1 shows the seasonal change of monthly average of NMHC value and Figure 2 shows the seasonal change of monthly average of NO_x value measured at A, B and C stations. The monthly average of NMHC value and NO_x value showed the tendency which will become high in November and in December at three measurement stations. This is result of ground inversion layer which is well known, it is made easily from the middle of November to the middle of December. It is because a migratory anticyclone overlies and the difference of temperature in a day is large in this period

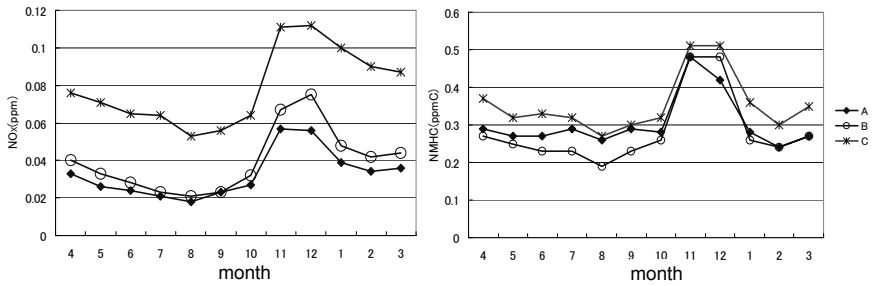


Fig.1 Seasonal Change of NO_x and NMHC concentration at A B and C station (fiscal year 2004)

Seasonal Change of the NMHC/NO_x ratio at A, B and C stations

Figure 3 shows seasonal transition of NMHC/NO_x ratio calculated by NMHC value and NO_x value measured at A, B and C stations and the monthly average temperature of Osaka in the 2004 fiscal year. .

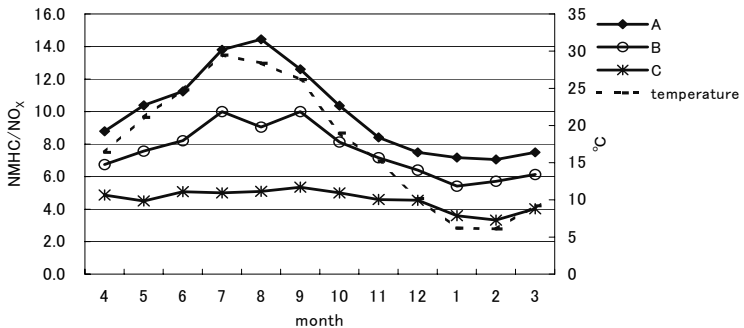


Fig.3 Seasonal Change of NMHC/NO_x ratio at A, B and C station and temperature at Osaka pref. (fiscal year 2004)

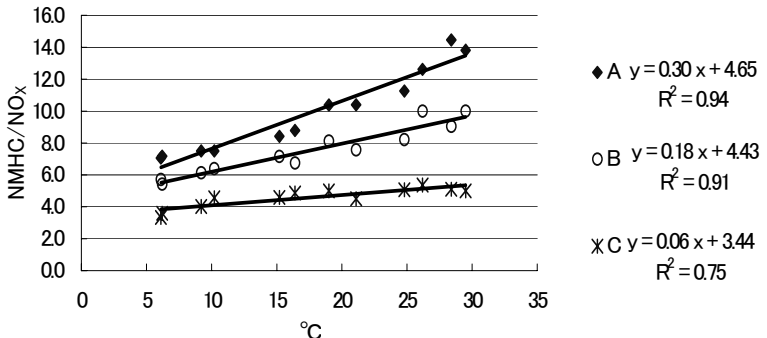


Fig.4 Correlation of NMHC/NO_x and Temperature in 2004 at A,B and C stations

As shown in Figure3. the influence of ground inversion layer was offset in October and December because both of NMHC and NO_x which discharged from fixed origin were similarly diluted and spread. Additionally, NMHC/NO_x ratio showed high value in summer (from June to September) at A and B stations but NMHC/NO_x ratio at traffic measurement station C was constant all year round. These results show that the amount of discharging NMHC and NO_x from emission sources around C station is not influenced from temperature and these are combustion origins. On the other hand, the amount of discharging NMHC from emission sources around A and B stations increased with rise of temperature. This is clearer than the linear regression equation of temperature and NMHC/NO_x ratio shown in the Figure4. This shows that there is NMHC source of non-combustion origin which is not managed in A city and B city, and A city has more such sources than B city. As example of such sources, industrial waste, waste plastics and any other nonburnable wastes which were piled up at outside are included. It is believed that a chemical reaction occurs by light or heat and various organic compounds are generated in such sources.

Annual change of NMHC/NO_x ratio at A, B and C stations

Annual transition of NMHC/NO_x ratio at A,B and C station from the 1997 fiscal year to the 2004 fiscal year are shown in Figure 5.

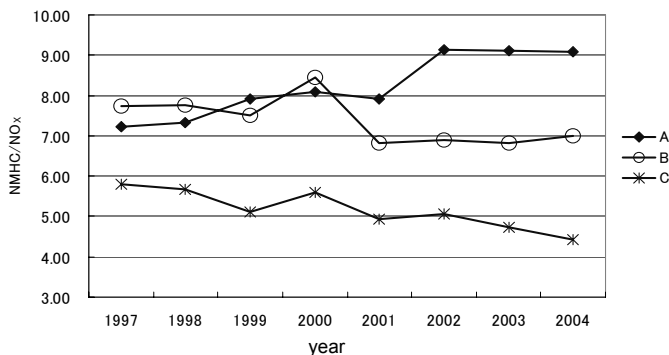


Fig.5. NMHC/NO_x ratio Change from the 1997 fiscal year to 2004 fiscal year at A, B and C stations

Most of NMHC and NO_x sources at C station which is traffic measurement station are cars, NMHC/NO_x ratio at C station is lower than A and B station which are public measurement stations. NMHC/NO_x ratio of A and B stations are about 8 from the 1997 fiscal year to the 2000 fiscal year, this shows that the amount of discharging NMHC from non-combustion origin of both is almost equal. Although, NMHC/NO_x ratio of A station begins to become higher than B station from the 2001 fiscal year, and is maintains the high ratio since the 2002 fiscal year.

In comparing the events at A city which is shown in Table1, the time which began the collection of waste plastics accords with the time when NMHC/NO_x ratio at A station became higher than B station. Moreover, correlation with operation of the waste plastic processing facility and increase of NMHC/NO_x ratio is seen, and it was reported that many kinds of VOC were generated when the waste plastics were accumulated, compressed and melted. The facility like this should be considered as emission sources of NMHC.

In the case of A city, it was noted that NMHC/NO_x ratio became high by construction of non-combustion origin.

Table1. The year of installation of waste disposal and treatment facility in A city

Year	Event
1980	Clean Center (incinerator) was completed
1994	Fracture facility(cans, glass and nonburnables) was completed
1998	PETbottles sorting, crushing and collection was started
2000	Spray cans and fluorescent collection was started
2002	Waste plastics collection and pressed bale packaging was started
2004	Test driving of the waste plastic processing facility was started
2005	Formal operation of the waste plastic processing facility was started

The influence that outdoor air gives indoor environment

As shown in Table2, the concentration of VOC and Carbonyl compounds were measured in the periphery of the waste plastic processing facility in A city.

Table2. TVOC and Carbonyls concentration in A city

I : From the facility to a 100m point II : From the facility to a 800m point

	June 23		June 24		June 26		June 27
	I	II	I	II	I	II	I
TVOC(by toluene)	256	71.6	308	38.2	717	239	193
Total Carbonyls	40.0	30.2	44.1	32.2	62.7	47.8	18.5

($\mu\text{g}/\text{m}^3$)

In this area, the concentration of TVOC exceeded $400 \mu\text{g}/\text{m}^3$ which was set as target level of indoor air quality by Health Labour and Welfare Ministry, although there was variation from day to day. This result shows that ventilation is not useful for the improvement of indoor air quality when outdoor pollution level is higher than indoors. These results show that discharged VOC should fully be examined about component identification and the control of discharging.

CONCLUSIONS

NMHC/NO_x ratio was proposed that becomes an index which evaluates change of regional environment by VOC discharged from non-combustion origin. The emission source of NMHC can be presumed without the influence of the diffusion and the dilution from the meteorological conditions by using NMHC/NO_x ratio.

At general measurement station of A city Osaka Prefecture, the NMHC/NO_x ratio shows high value in summer though NMHC and NO_x concentration show high value in early winter, but traffic measurement station C doesn't show this pattern. From these results, the amount of NMHC discharged from emission sources around A and B station was increased with rise of temperature. This shows that there is NMHC source of non-combustion origin which is not managed in A city and B city, and A city has more such sources than B city.

Annual transition of NMHC/NO_x ratio calculated using the value of NMHC and NO_x measured at A,B and C stations were compared. At A station, NMHC/NO_x ratio increased with collection of waste plastics and operation of the waste plastic processing facility, and it was presumed that the facility like this was one of the non-combustion origins discharging NMHC.

The concentration of VOC and Carbonyl compounds were measured in the periphery of the waste

plastic processing facility which presumed to be non-combustion origin of NMHC. There is the day when TVOC concentration exceeds $400\mu\text{g}/\text{m}^3$ (target level of indoor air), it means that ventilation is not useful for the improvement of indoor air quality. In this case, it is believed that the identification and the control of discharged VOC are required.

In conclusion, the transition of NMHC/NO_x ratio shows that change of the regional environment polluted by VOC can be evaluated and the influence on indoor environment can be presumed.

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