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Determination of Carcinogenic and Endocrine Disrupting Chemicals in Airborne Particulates

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1. Introduction:

Urban air polluted with diesel exhaust particulates (DEP) is a cause of lung cancer. Extracts from DEP obtained with organic solvents contain carcinogenic and/or mutagenic polycyclic aromatic hydrocarbons (PAHs) and nitropolycyclic aromatic hydrocarbons (NPAHs) such as benzo[a]pyrene (BaP) and 1,8-dinitropyrene (1,8-DNP), respectively. Recently, it has been reported that inhalation of DEP affects the male reproductive system in rats and mice. We have found that extracts from DEP showed both antiestrogenic and antiandrogenic effects and that a part of the activities was originated from PAHs. As a main contributor of PAHs and NPAHs, automobiles have been considered. These facts suggest that the determination of PAHs and NPAHs in urban air is very important.

2. Determination method:

Many studies using HPLC with fluorescence detection or GC/MS have been reported for the determination of PAHs. On the other hand, NPAHs have been little studied in spite of the strong direct-acting mutagenicity, mainly because their atmospheric concentrations are much lower than those of PAHs. PAHs are sensitive to fluorescence detection. Moreover, NPAHs are chemically reduced to their corresponding amino-derivatives which are sensitive to not only fluorescence but also peroxyoxalate chemiluminescence detection. We developed a highly sensitive HPLC method for NPAHs with fluorescence and chemiluminescence detection. The detection limits were at sub femtomole levels, which are two orders of magnitude lower than those by HPLC with fluorescence detection or GC/MS. Utilizing this method, we determined several NPAHs such as 1,3-, 1,6- and 1,8-DNPs and 1-nitropyrene (NP) in a sub milligram of automobile exhaust and airborne particulates. By introducing a Pt/Rh reducer column and a switching valve in to the HPLC system, both PAHs and NPAHs in particulates have been determined simultaneously after simple clean-up treatments [1-3].

3. Atmospheric behaviors and contributors:

Airborne and automobile exhaust particulates were collected. When airborne particulates were collected simultaneously at downtown and suburban sites in several Japanese cities, the mean atmospheric concentrations were lower at the suburban sites. The difference in the PAH concentrations in particulates was smaller between the two sites in spite of the larger difference of particulate concentration. However, the difference in NPAH concentrations in particulates between the two sites was greater, suggesting that the NPAHs were less stable. The concentrations of 1-NP and 1,3-, 1,6- and 1,8-DNPs were much higher in automobile exhaust particulates than in airborne particulates. Analytical results suggested that main contributors of these compounds in urban air were diesel engine vehicles. However, several NPAHs such as 2-nitrofluoranthene (2-NFR) and 2-NP were not observed in DEP but in airborne particulates and showed different diurnal concentrations. From these results, the atmospheric formation of 2-NFR and 2-NP was considered. However, airborne particulate samples collected in Vladivostok showed different chromatographic patterns, suggesting that other large contributors such as power plant and domestic heating which consume coals were also considered [4-7].

4. Mutagenicity:

When airborne particulates were collected by using an Andersen high-volume air sampler, the NPAH concentrations were highest in the finest particulate fraction (< 1.1 um) in which DEP were main components. If the effect of coexisting compounds is assumed to be negligible, more than 1/3 of the direct-acting mutagenicity of airborne particulates could be attributed to this fraction in the Ames test using the Salmonella typhimurium strain. When the DEP extracts were separated into five fractions by silica-gel column chromatography with hexane, hexane/dichloromethane, dichloromethane and ethanol, the strong direct-acting mutagenicity was observed in the dichloromethane fraction (almost 2/3) and in the ethanol fraction. More than 1/2 of the activity in the former fraction was attributed to only four NPAHs, 1-NP and 1,3-, 1,6-and 1,8-DNPs [8-10].

5. Endocrine disrupting activity:

An antiestrogenic activity of the DEP extracts was observed in the estrogen-responsive MCF-7 cells and an antiandrogenic activity of DEP extracts was also observed in the androgen-responsive PC-3/AR cells. Several PAHs such as BaP showed both activities, suggesting that a part of the endocrine disrupting activities of DEP might be attributed to PAHs through an aryl hydrocarbon receptor-binding process. We also found that several hydroxylated metabolites of PAHs such as 3-hydroxybenzo[a]pyrene bound to estrogen receptors and that Cytochrome P450

1A1 production was induced by BaP. This process may also contribute to the disrupting activity of DEP [11, 12].

6. Personal exposure:

Concentrations of PAHs and NPAHs are much higher than those of dioxins in the urban air. Although the proposed method can determine atmospheric PAHs and NPAHs, it is not easy to know the personal exposure. Determination methods for these compounds and metabolites in biological samples should be established for the risk assessment.

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