ABSTRACT
The dusts on road surfaces in urban areas contain polycyclic aromatic hydrocarbons (PAHs) exhausted from automobiles. PAHs in the dusts seem to be runoff into the aqueous environment together with the dusts on rainy days. In Japan, trunk roads are swept by street sweeping trucks periodically. 7 trunk road sections within Okayama Prefecture, Japan were selected. The dusts under 750 μm in the road refuse were obtained with a sieve. The concentrations of the PAHs included in the dusts under 750 μm were analyzed once a month. The PAHs analyze were 8 kinds of chemical compound such as benzo(a)pyrene, phenanthrene and fluoranthene. The runoff loads of 5 chemical compounds were investigated. In this study, the runoff loads of 5 compounds within 8 compounds analyzed were estimated using numerical simulations. The temporal changes of both the street dust amounts and the PAHs amounts in the dusts were expressed by differential equations, respectively. The calculation results show the good reproduction of observed dust amounts and the concentrations of the PAHs in the dust. The emitted PAHs on the road surfaces from automobiles seem to decompose by solar radiation considerably, and the road sweeping is effective for reducing the runoff loads of PAHs into the aqueous environment for roads in the region where the decomposition by solar radiation is not so much.

Key words: analysis of PAHs, runoff loads from road surfaces, numerical estimation

INTRODUCTION
Polycyclic aromatic hydrocarbons (PAHs) exist in dusts on urban road surfaces. The origins of these PAHs are considered to be automobile exhaust, lubricating oils, atmospheric depositions and so on. PAHs are toxic and one important source of PAHs into the aqueous environment is road runoff (Degirmenci, E. et al., 2000). The PAHs amounts on road surface change due to following phenomena. PAHs are exausted from motor vehicles and carried away by wind and traffic. The dusts on road surfaces are washed by rainfall and PAHs in the dusts runoff into the aqueous environment. The solar radiation decomposes PAHs in dusts. Furthermore, the trunk roads are swept by street sweeping trucks periodically in Japan. In this study, we investigated the runoff amounts of PAHs from road surfaces based on the observed concentrations of PAHs and dust amounts. As the behavior of PAHs on road surface is very complicated, the runoff amounts of PAHs are estimated using a numerical simulation.
**Observation**

Seven trunk road sections within Okayama Prefecture, Japan were selected. Fig. 1 shows the selected road sections within Okayama Prefecture. Each road section is divided into several road subsections for convenience of road sweeping work, and a street sweeping truck sweeps each subsection by at least once a month. The swept refuse from each road subsection was mixed with the refuse from other road subsections in the same road section. Certain amounts of the swept refuse from 7 trunk road sections were air-dried in the laboratory, and then the coarser fractions in the refuse such as gravels, woodchips and cigarette ends were removed. The dusts under 75µm in the refuse were obtained with a sieve. The concentrations of the PAHs included in the dusts under 75µm were analyzed once a month. The PAHs analyzed were 8 kinds of chemical compound such as benzo (a) pyrene, phenanthrene and fluoranthene. Here, 5 compounds of 8 observed compounds were investigated in order to estimate the runoff loads into the aqueous environment.

Addition to the concentrations of the PAHs in the road dusts, the data of the swept dust amounts, sweeping date, daily precipitation, daily sunshine duration, traffic volumes on each road section were collected from October, 1998 to November, 1999, and used for the runoff estimation of the PAHs.

**Method of Numerical Estimation**

The runoff loads of the PAHs cannot directly be estimated from the PHAs concentrations in the dusts and the swept dust amounts. For the direct estimation, the observations of PAHs in the rainfall are needed. But these observations are very difficult. Therefore, the runoff loads of PAHs are estimated from the differences between the amounts on road surfaces just before rainfall and those just after rainfall using a numerical simulation.

The street dust amounts and the PHAs concentrations in the dusts are assumed to change as the following (Novotny, V. and Olem H, 1994). The street dust amounts increase due to 1) total traffic and atmospheric deposition, and decrease due to 2) carry away by wind and total traffic and 3) runoff by precipitation. The amounts of the PAHs in the dusts increase due to 4) the PHAs emitted mainly from motor vehicles with diesel engines, and decrease due to 5) decomposition by solar radiation, 6) runoff by precipitation together with the dusts, 7) carry away by wind and total traffic together with the dusts and 8) sweeping roads. The PAHs are poorly soluble in water, and have a tendency to runoff together with small particles and organic substances. Therefore, the behavior of the dusts is important to the runoff of the PAHs to the aqueous environment.

According to the assumptions mentioned above, the amounts of dusts and PAHs in dusts are expressed as Equation (1) and Equation (2), respectively. Here, the influence of wind is neglected because the selected trunk roads have heavy traffic volumes and the influence of carry away by traffic seems to be dominant.

\[
\frac{dS}{dt} = k_1 Tr - k_2 S Tr - k_3 SR^a
\]

(1)

\[
\frac{d(PS)}{dt} = k_4 Tr_p - k_2 S Tr - k_3 SR^a P - k_3 SPI
\]

(2)

Where, S: amount of dust on road surface of unit area,
TRD: traffic volume of motor vehicle with diesel engine,
TR: total traffic volume of motor vehicle,
R: daily precipitation
I: product of daily sunshine duration and sunshine intensity
k1~k5, a: constant.

The temporal changes of both the street dust amounts and the PAHs amounts in the dusts are expressed by differential equations, respectively. These two differential equations include several unknown parameters. These unknown parameters in the equations were estimated to reproduce the PAHs concentrations in the swept dusts and the swept dust amounts.

**RESULTS AND DISCUSSION**

The calculation results of estimating observed dust amounts and observed concentrations of PAHs in the dusts are shown in Fig. 2 to Fig. 7. The calculation results show the considerably good reproduction of observed dust amounts and the concentrations of the PAHs in the dust. The regression equations shown in the figures represent relations between calculations (x) and observations (y). The reproducibility is higher, as the gradient of the regression line and R^2 are nearer for 1. Fig. 8 shows the precipitations and durations of sunshine used for the simulation. The typical results of simulated daily variations of the dust on the road surfaces and phenanthrene amounts on the road surfaces are shown in Fig. 9. The results shown in Fig. 9 are the variations in one road subsection for Sample 1.
Fig. 2 Comparison of swept dust amounts between calculations and observations

Fig. 3 Comparison of swept benzo (a) pyrene amounts between calculations and observations

Fig. 4 Comparison of swept phenanthrene amounts between calculations and observations

Fig. 5 Comparison of swept fluoranthene amounts between calculations and observations

Fig. 6 Comparison of swept pyrene amounts between calculations and observation

Fig. 7 Comparison of swept benzo (a) anthracene amounts between calculations and observations

y = 1.296x
R^2 = 0.551

y = 1.13x
R^2 = 0.79

y = 1.202x
R^2 = 0.79

y = 0.837x
R^2 = 0.838

y = 1.573x
R^2 = 0.878
The dust amounts approach saturation amounts without precipitation and road sweeping, and decrease due to precipitation and road sweeping. The phenanthrene amounts vary even when the dust amounts monotonously increase. These variations of phenanthrene amounts depend on the durations of sunshine. Ozaki et al. (1999) obtained the phototransformation rate constants of PAHs assuming that the transformation reactions are first order. The rate constants range from 0.05 to 0.2 (1/d). These rate constants mean that the original concentrations of PAHs become half in 3.5 days to 2 weeks. The considerable amounts of PAHs seem to be transformed to other compounds on road surfaces during sunny days before runoff.

Based on the numerical simulation, the amounts of the runoff into the aqueous environment, the decomposition by solar radiation on the road surfaces and the removal by road sweeping are estimated. The estimated amounts of decomposition by solar radiation occupy 30-90 percents in the total emitted PAHs. The decomposition amounts are 80-90 percents in many cases, and the amounts of runoff and removal by road sweeping are not so much. But the decomposition amounts are rather little for the road sections in the region with many rainy days. Both the runoff amounts and swept amounts are of nearly equal degree in these road sections. Therefore, the road sweeping is effective for reducing the runoff of PAHs in rainy region.
As the observation frequency of PAHs is not so enough, the obtained results are qualitative. The important tendency on the runoff loads of PAHs is clarified. The decomposition by solar radiation plays a very important role for reducing the runoff amounts of PAHs.

CONCLUSIONS
Based on both the observations of PAHs and the numerical simulations, the runoff amounts from road surfaces into the aqueous environment were estimated. According to the estimation, the emitted PAHs from automobiles are mainly decomposed on the road surfaces by solar radiation before runoff. The decomposed amounts depend on solar radiation. The removal of PAHs by road sweeping is important in the region with many rainy days in order to reduce the runoff amounts of PAHs into the aqueous environment.

REFERENCES