SEASONAL CHANGE OF POPS CONCENTRATIONS IN AMBIENT AIR ON NIIGATA AREA JAPAN

Hitoshi Murayama[1,2], Yuuya Takase[2], Hideko Mitobe[1], Toshiyuki Aoki[1], Hiroyuki Mukai[1], Masaharu Ohzeki[1], Ken-ichi Shimizu[2] and Yoshie Kitayama[3]

[1]Niigata Prefectural Institute of Public Health and Environmental Sciences, 314-1 Sowa, Niigata 950-2144, Japan
[2]Graduate School of Science and Technology, Niigata University, 8050 Igarashi-2-nocho, Niigata 950-2181, Japan
[3]Department of Chemistry and Chemical Engineering, Faculty of Engineering, Niigata University, 8050 Igarashi-2-nocho, Niigata 950-2181, Japan

Introduction

The use of POPs including PCBs and organochlorine pesticides were prohibited in Japan in the 1970s, although a great deal of PCB-containing waste is still left untreated. Just recently, it was discovered that great quantities of organochlorine pesticides, such as DDT and HCHs, are stored all around Japan. Some organochlorine pesticides are still being used in parts of the world, which could lead to the environmental pollution of the neighboring regions, or even the entire world. There have been lots of studies conducted on the water environment, but very few on the atmosphere, so little pertinent information is available on these concerns. Niigata Plain, one of the main rice production areas in Japan, was a suitable place for investigating the former uses and the migration from other countries. Five sites in the plane were selected for monitoring the POPs between September 1999 and November 2001. By identifying the factors that contribute to varying concentration, existences of the emission sources in the surrounding area were consulted.

Experimental

Ten chemicals, including hexachlorobenzene (HCB), α-, ß-, γ- and δ-hexachlorocyclohexane (HCH), trans- and cis-chlordane (CHL), p,p'-DDE, p,p'-DDD and p,p'-DDT, were selected for the study. The sampling locations are shown in Figure 1. YAHIKO is located in the remote area near the top of Yahiko Mountain, 586 meters above sea level. Other four sites are scattered in the plane. NIIGATA is situated at the site of our Niigata laboratory, in a suburb of the Niigata city. Active carbon filter paper was employed for sample collection[1]. Air was continuously sucked through the filters for seven days (100 m^3) to collect the POPs in air. This procedure was repeated every week throughout the period of study. The POPs collected on ACFP were extracted, purified with florisil and analyzed by HRGC-HRMS. The extraction and analytical method in detail were described in previous reports[1,2]. The detection limits were determined as follows: 1 pg/m^3 for HCB, trans-and cis-CHL; 2 pg/m^3 for α-, ß-, γ-HCH, p,p'-DDD and p,p'-DDT; 4 pg/m^3 for d-HCH; 0.3 pg/m^3 for p,p'-DDE.

Results and Discussions

POPs concentration levels at each site

The mean values of the POPs concentration in the atmosphere, measured at NIIGATA, TSUBAME, and MAKI from June to September 2000, and measured at NIIGATA, JOHZO, and YAHIKO from

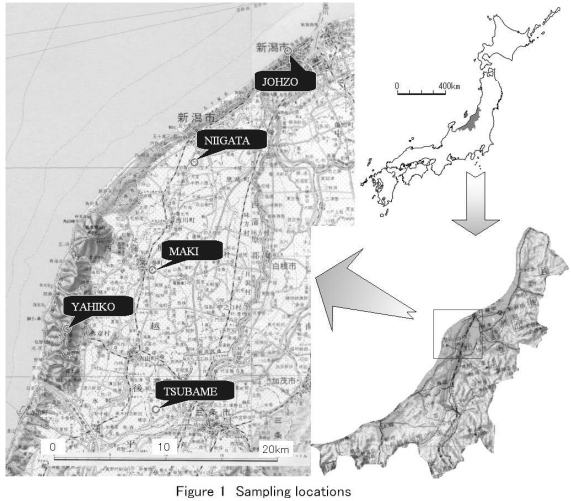


Figure 1 Sampling locations

May to November 2001, were shown in Figure 2 and 3, respectively. The vertical axis is logarithmic. p,p'-DDD was detected at none of the sites and thus is not shown in the figure. Among the 3 sites measured in 2000, TSUBAME showed slightly higher values in CHLs than the other two, as shown in Figure 2. Except for that, almost equal levels of concentration were observed for all the substances. This is considered to occur because the three sites are all located in the suburbs, and all the sites shared similar characteristics. In contrast, the three sites measured in 2001 (NIIGATA, JOHZO, and YAHIKO) showed major differences in concentration (Figure 3). In YAHIKO, although there was only a slight difference in the concentrations of α-HCH and γ-HCH from those in the other two sites, the concentrations of all the other substances were low. Particularly, the concentrations of ß-HCH, trans- and cis-CHL, and p,p'-DDT were different. Supposedly this was because at YAHIKO the samples were collected at the mountaintop, which was 586 m above sea level, and very far from both the urban areas and agricultural areas at the foot of the mountain. Possibly this remote situation allowed the concentration of the pollutants to decrease via dilution and/or adsorption during transport. The concentrations of CHLs were relatively high at TSUBAME and JOHZO, because these sites are neighboring residential areas, which might be a source of CHLs due to the past usage of them as termiticide. In the studies of 2000 and 2001, the concentration level of a and g-HCH were similar at all the sites and hardly differed among the regions. This suggests that these substances are pollutants mostly resulting from long-range transport.

The concentration levels of the same period (June to September) at NIIGATA were compared between 2000 and 2001, and the results are shown in Figure 4. The concentrations of a and γ-HCH in 2001 were similar to those in 2000. POPs other than those decreased by 20 % (DDT) to 59 % (b-HCH). The environmental half-lives of POPs are reported to be several years (1.8 - 22 years) according to the long-term observation of atmospheric concentration[3-5]. Therefore, the decrease observed during the period between 2000 and 2001 may reflect the tendency of natural decrease in the concentration of POPs, since the use of organohalogen pesticides has been prohibited in Japan over 20 years ago.

Seasonal variation of the atmospheric concentration

At NIIGATA, the atmospheric POPs concentrations were investigated consecutively for over 2 years from September 1999 to November 2001. Seasonal variation of the atmospheric concentration

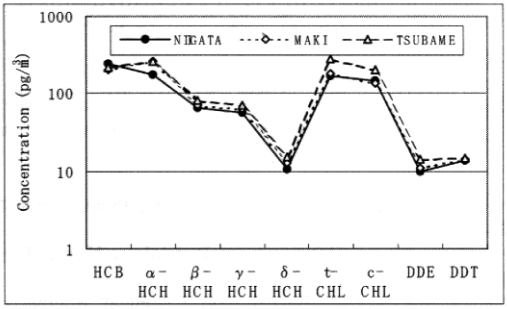


Fig. 2 Arithmetic mean concentration of POPs measured in NIIGATA, MAKI, TSUBAME during June- September, 2000

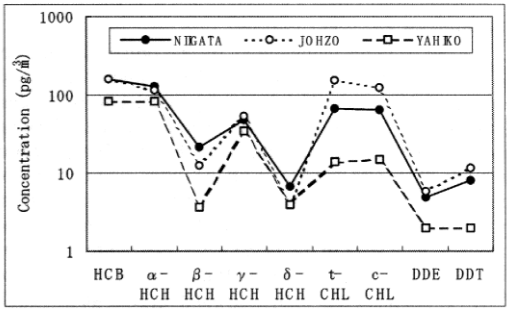


Fig. 3 Arithmetic mean concentration of POPs measured in NIIGATA, JOHZO, YAHIKO during May- November, 2001

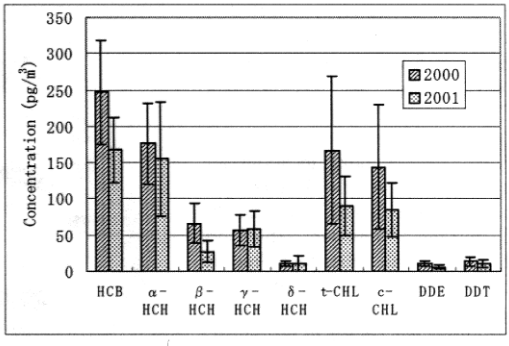
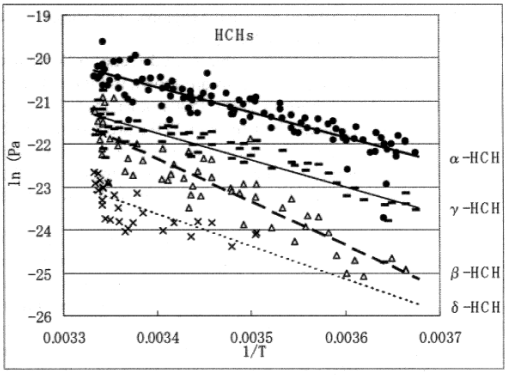
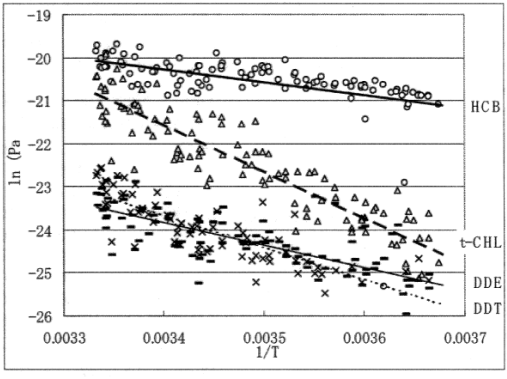


Figure 4. Comparison of mean concentrations between 2000 and 2001during June- September at NIIGATA



(A) α, β, γ and δ-HCHs



(B) HCB, trans-Chlordanes, p,p'-DDE and p,p'-DDT

Figure 5. Clausius-Clapeyron plot of POPs

Table 1. Measured temperature dependence of POPs

POPs	n	m	b	r^2	
HCB	106	- 2,210	10	0.459	<0.001
ƒ ¿HCH	107	- 5,840	- 1	0.779	<0.001
ƒ ÀHCH	59	- 10,200	12	0.820	<0.001
ƒ ÁHCH	63	- 6,240	- 1	0.788	<0.001
ƒ ÂHCH	29	- 7,570	2	0.462	<0.001
trans- CHL	106	- 10,800	15	0.815	<0.001
cis- CHL	106	- 10,700	15	0.812	<0.001
p,p'- DDE	103	- 5,250	- 6	0.550	<0.001
p,p'- DDT	80	- 7,380	1	0.694	<0.001

Given is the slope m of the relationship ln (Pa) = m (1/ T) + b, the number of observations n, the regression r^2

was observed for all the POPs. The concentrations were low in winter and high in summer according to the temperature. These results indicate that the concentrations in air are strongly affected by the temperature. Therefore we applied the results at NIIGATA to the following Clausius-Clapeyron (CC) equation.

$$1n\ (Pa) = m/T + b \qquad (i)$$

As shown in Figure 5, a high correlation was observed for all the POPs with a level of significance of $p<0.001$. The slope m, the intercept b, the regression coefficient r^2 and the level of significance p are summarized in Table 1. Among the POPs, HCB had the smallest slope and r^2, indicating that the atmospheric concentration of HCB was affected by both the long-range transport[6] and the local source such as incinerator. On the contrary, chlordane had a largest slope, indicating that chlordane might be generated from the surrounding residential area.

Among the HCHs, the slope was larger in the order of ß>δ>α≈γ. b-HCH could be affected more by what is remaining in the surrounding area, rather than by the long-range transport. Possibly this is because technical HCHs had been widely used in Japan, and only ß-HCH remained in the environment due to the low vapor pressure and high stability.

References

1. Mitobe, H.; Murayama, H.; Mukai, H.; Moriyama, N. *J. Environ. Chem*. 2001, 11, 477-489.
2. Murayama, H.; Tanabe, A.; Mukai, H.; Moriyama, N. *Bunseki Kagaku* 2001, *50*, 537-545.
3. Haugen, J.-E.; Wania, F.; Ritter, N.; Schlabach, M. Environ. Sci. Technol. 1998, 32, 217-224.
4. Corts, D. R.; Basu, I.; Sweet, C. W.; Brice, K. A.; Hoff, R. M.; Hites, R. A. Environ. Sci. Technol. 1998, 32, 1920-1927.
5. Bidleman, T. F.; Jantunen, L. M.; Falconer, R. L.; Barrie, L. A. Geophys. Res. Lett. 1995, 22, 219-222.
6. Wania, F.; Haugen, J.-E.; Lei, Y. D.; Mackay, D. Environ. Sci. Technol. 1998, 32, 1013-1021.