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Monitoring of Urinary Alkyl Phosphates in Pest Control Operators Exposed to Various Organophosphorus Insecticides

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Several organophosphorus insecticides have been used in Japan for pest extermination and termite control in house constructions since 1986, when the usage of chlondane was prohibited. Therefore, a monitoring study was conducted regarding daily excretion levels of alkyl phosphates, major urinary metabolites in pest control operators (PCOs) exposed to these insecticides, in order to investigate their actual intake of the chemicals during their routine work.

Biological monitoring of urinary alkyl phosphates has been applied to the studies of exposure assessment and health hazard of organophosphorus insecticides in occupational workers (Hayes et al., 1980, Franklin et al., 1986, Vasilić et al., 1987, Jauhiainen et al., 1992).

In this study we examined 1) ordinary urinary levels of diethyl phosphate (DEP) and dimethyl phosphate (DMP) in PCOs exposed to three kinds of these insecticides; fenitrothion plus dichlorvos, pyridaphenthion and chlorpyrifos, 2) daily fluctuations of urinary DEP or DMP values as the indicator of exposure in PCOs during a one-week study period and effect of interruption period of exposure on fluctuations of the indicators.

MATERIALS AND METHODS

The subjects were six male PCOs, between 22 and 46 years old belonging to three firms. They collected about 10 ml urine from the first urine voided in the morning into a polyethylene test tube every day for a week and these specimens were maintained at -20°C until analysis of alkylphosphates. Urine specimens were collected between Nov. 15 and Dec. 16, 1992.

Ion-exchange amberlite CG 120 resin (H^+ form) (Organo Co., Tokyo, Japan) was prepared by drying at 120℃ for 30 minutes (Daughton et al. 1979) after elution with distilled water and acetone. Creatinine in the urine was determined by the kit reagent (Wako Pure Chemical Industries, Osaka, Japan). Urinary DMP and DEP concentrations were adjusted to the creatinine content (Davies et al. 1982). The procedure for determining dialkyl phosphate (DMP and DEP) in the urine was as follows. Inorganic phosphate was removed by addition of $Ca(OH)_2$ to each urine sample (5 ml). After centrifugation, the supernatant fluid was purified by passage through a pipette packed with 1.0 g of the dried resin. The pH of the eluate (4 ml) was neutralized with 1N $NaHCO_3$. The alkyl phosphate residues in a definite amount of the fluid were derivatized by the pentafluorobenzyl (PFB) reaction, which was performed using one half the amounts of reagents described in the method of Reid and Watts (1981) and the reaction products were determined by GC chromatography. A Hitachi Model 663 gas chromatograph equipped with a flame photometric detector was operated in the phosphorus mode. The GC column was glass (2.0 m by 3 mm i.d.) packed with 4% SE-30 and 6% OV-210 (Gass Chrom Q, 80-100 mesh). The operating conditions were as follows; injector, oven and detector temperatures were 220℃, 180℃ and 230℃, respectively. Carrier gas (N_2) flow rates, 60 ml/min; pressures were 1.0 kg/cm^2 for hydrogen and 1.8 kg/cm^2 for air.

RESULTS AND DISCUSSION

The present recovery of DMP from 5 urine samples fortified at 1.0 ppm and DEP at 0.50 ppm was 132 ± 23% and 149 ± 9%, respectively. These high recoveries in both cases indicate that some factors derived from urine promote the derivatization reaction of the alkyl phosphates.

Subject No. 1 engaged in spraying with a combined emulsifiable concentrate of fenitrothion and dichlorvos to exterminate cockroaches in house constructions and preparing the insecticide solution during the study period. The maximum DMP of 0.13 μg/mg creatinine was observed on both the 6th and 7th days. The level dropped on the 4th and 5th days to that below the threshold of detection, demonstrating the effect of interruption of his exposure to the insecticides during the previous two days. Subject No. 2 belonged to the same firm as subject No. 1, conducted primarily mixing of the chemicals during the study period. The decrease of DMP value from the second to 4th day is considered due to previous interruption of exposure for two days, as for subject No. 1.

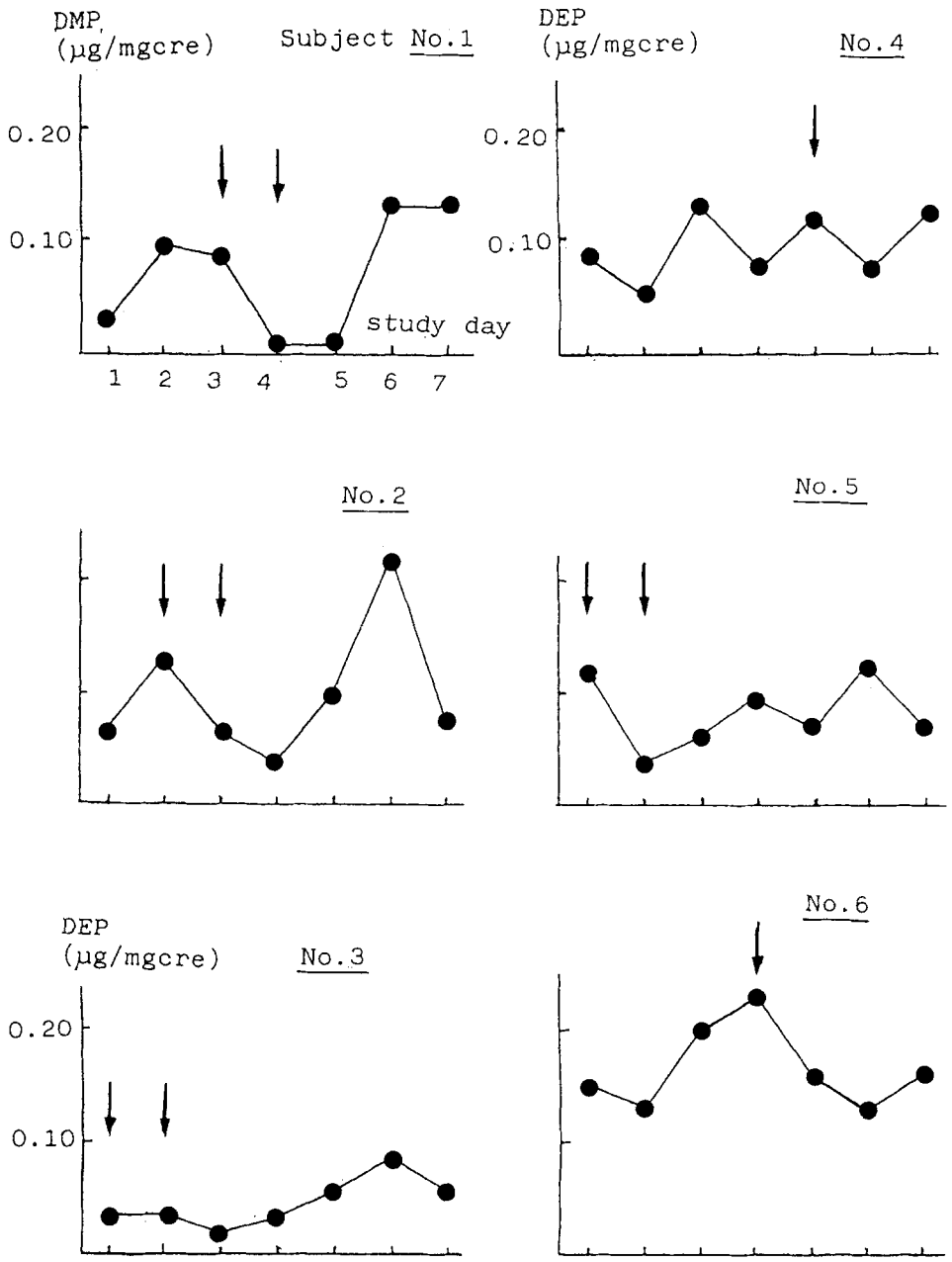

Figure 1. Daily urinary fluctuations of DMP and DEP during the study period.
Arrow indicates non-working day.

Table 1. Alkyl phosphate levels in urine excreted from PCOs exposed to organophosphorus insecticides

No.	Organophosphorus insecticides	Range (μg/mg creatinine)	Mean ± SD* (μg/mg creatinine)	C.V.* (%)
1	0.5 % fenitrothion plus	ND** - 0.13	—	—
2	0.2 % dichlorvos	0.040 - 0.22	0.099 ± 0.060	60.6
3	1.6 % pyridaphenthion	0.020 - 0.087	0.046 ± 0.022	47.4
4		0.052 - 0.13	0.094 ± 0.030	31
5	1 % chlorpyrifos	0.040 - 0.125	0.083 ± 0.031	37
6		0.13 - 0.23	0.165 ± 0.036	21.8

Monitoring index is DMP for No.s 1 and 2, DEP for No. 3-6.
* : determined for one week including non-working day.
** : < 0.02 ppm

Subject No. 3 was primarily spraying pyridaphenthion for termite control. A gentle fluctuation curve of DEP was observed for a week. No definite effect of the first two days of interruption of his work was observed on the following daily fluctuations of DEP values.

Three workers, No. 4-6, who belonged to the same firm, used similarly chlorpyrifos for termite control. Subjects No. 4 and 5 showed an average DEP level of about 0.1 μg/mg creatinine during the study week, and no definite effect of work interruption for one or two days was found on the subsequent values of the indicator. Subject No. 6 showed an average DEP value twofold as high as those of the previous two workers (table 1). The decrease in DEP level observed from 4th to 6th day indicates that it might have been produced by interruption of work on the 4th day. These findings demonstrate that the urinary excretion rate of DEP derived from chlorpyrifos or pyridaphenthion is slow as compared to those of DMP from dichlorvos and fenitrothion. According to Vasilić et al. (1992), urinary DEP excretion kinetics of acute patients intoxicated with chlorpyrifos showed a biphasic pattern, and their half time in slow phase of DEP excretion is 98-104 hr. Morgan et al. (1977) reported that the urinary rate of DEP excretion following ingestion of ethyl parathion in human subjects is slower than that of DMP from methyl parathion ingestion.

The coefficient of variation (C.V.) of DEP or DMP in the one-week study period concerning three subjects No. 2, 3 and 5, who did not work for two days, but were exposed to different insecticides is 60.6, 47.7, 37, respectively (table 1) The C.V. value of subject No. 5 exposed to chlorpyrifos was smaller than that of the others. Moreover, the C.V. of DEP on subjects No. 4 and 6 who did not use chlorpyrifos for one day was 31 and 21.8 respectively and smaller than that of No. 5 who did not work for two days. Consequently, these C.V. values reflect the urinary rate of DEP or DMP excretion from these insecticides in PCOs and the effect of the period of interruption of work on the fluctuations of DMP or DEP levels during the study period.

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