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Determination of Dialkyl Phthalates in High Altitude Atmosphere for Validation of Sampling Method Using a Helicopter

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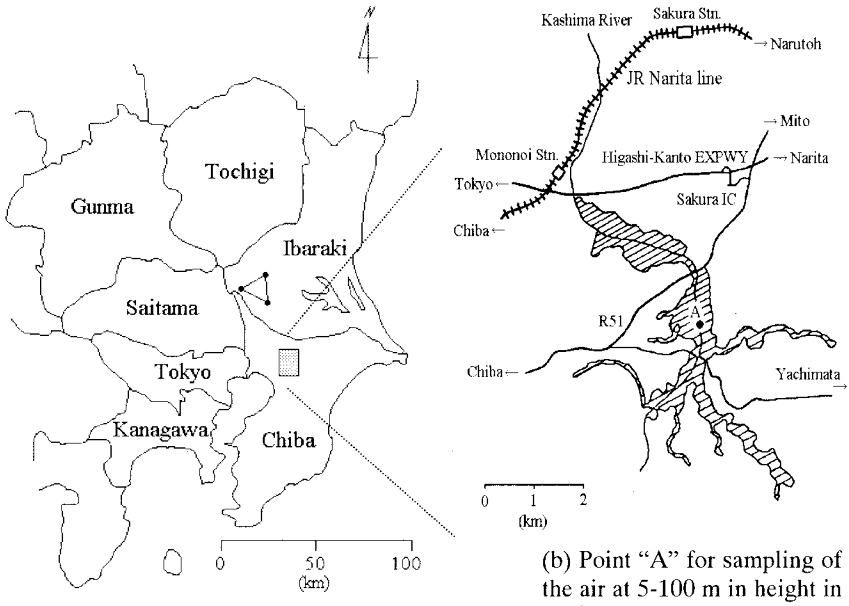
Dialkyl phthalates are mainly used as plasticizers of polyvinyl chloride; the annual producing amounts of di(2-ethylhexyl) phthalate (DEHP) were 248,995 t in 1984, 261,219 t in 1987 and 273,375 t in 1988 (The Chemical Daily Co., Ltd. 1986, 1989, 1990), whose amounts were gradually increasing with year. The concentrations of DEHP and di-n-butyl phthalate (DnBP) in the atmosphere were 0.32-2.68 ng/cu m and 0.40-1.80 ng/cu m, respectively, at 18 m in height from April to August, 1979 in the north Pacific Ocean as background level (Atlas et al. 1981). The atmospheric concentrations of DEHP and DnBP were 25-60 ng/cu m and 27-36 ng/cu m in February, 1976 at an urban site in Japan (Yamasaki et al. 1977), and the concentrations of DEHP and DnBP were 38-790 ng/cu m and 17-370 ng/cu m, respectively, over the urban or rural area in summer, 1985 in Japan (Environment Agency of Japan 1986). However, the concentrations of dialkyl phthalates at high altitude have been rarely reported because of the difficulty of sampling. And it is reported that dialkyl phthalates have been suspected to be an endocrine disrupter (Colborn et al. 1996; Cadbury 1997; Environment Agency of Japan 1998), and also the residues of dialkyl phthalates in the environment have been a matter of the public concern.

We sampled the air at 5-100 m and at 150-800 m in height of altitude in 1992 and 1991, respectively, at Kanto Plane in Japan. Pesticide concentrations in these samples were determined with GC/MS (SIM: Selected Ion Monitoring) (Watanabe 1996, 1998). The maximum concentrations of fenitrothion and fenobucarb were about 0.6 to 0.8 μg/cu m at 5 m in height and about 0.1 to 0.4 μg/cu m at 100 m in height on the sprayed day, when they were sprayed on a rice plant in paddy field. It was observed that the pesticide concentration was decreased with rising in altitude. The concentrations at 5-100 m in height of 46 pesticides, which were not sprayed on that day, were below the detection limits of 0.05-0.1 μg/cu m. And also the concentrations of 47 pesticides at 150-800 m in height over the paddy field area were below the detection limits of 0.005-0.05 μg/cu m. The air over 30 m of altitude was sampled using a pilot-boarding helicopter or radio-controlled one. Then, these samplings were possible to be affected by down wind accompanied with revolving of a rotor of helicopter. Based on the fact that



(b) Point "A" for sampling of the air at 5-100 m in height in Chiba Prefecture.

(a) Flight course of helicopter for air sampling at 150-800 m altitude (●——●).

Figure 1. Map of air sampling area

dialkyl phthalates were usually determined in the air on the surface of ground, our sampling method using a helicopter was validated by detecting the phthalates in the atmosphere as an indicator in columns.

MATERIALS AND METHODS

As the standards of dialkyl phthalates and adipate (both of which are abbreviate to DAPs, hereafter), NR (Normal Reagent), GR (Guaranteed Reagent) or Reagent grades from Tokyo Kasei Kogyo Co., Ltd. were used for the analysis of these esters, and they are listed in Tab. 4. For the solvent was used PR (Pesticide Residue) grade or GR grade from Wako Pure Chemical Industries. Diethylene glycol (DEG) of EP (Extra Pure) reagent from Kanto Chemical Co., Inc. and silica gel column of Waters Associates SEP-PAK SILICA were also used in the analysis.

Air was sampled at 1.5 m, 5 m, 30 m, 50 m and 100 m in height on point "A" in Chiba Prefecture on August 1, 1992 (Fig. 1(b)). 100 L volumes of air at 1.5 m and 5 m in height were sampled at the rate of 1.2 L/min for 30-40 minutes with two sets of silica gel columns, which were bound to a pole and pumps (Shibata MP-601T). Air volume was measured with a dry gas meter (Shinagawa-Seiki DK-2Cf-T). Four sets of silica gel columns and pumps with batteries were hung under the radio-controlled helicopter (Yamaha Model R-50; body length 2.7 m

Table 1. Meteorological conditions for air sampling on July 23, 1991

	altitude			
	150m	300m	500m	800m
sampling time	9:40-10:15	10:45-11:20	13:30-14:10	15:05-15:40
weather	fine	fine	fine	fine
temp. at indoor(°C)	31	32	34	34
temp. at outdoor(°C)	28	26	28	27
wind speed	weak	breeze	calm	breeze
wind direction	S	S	S	S
pressure(hPa)*	995	977	955	921
visibility	good	good	not good	good

*: The pressure of each altitude at outdoor of the helicopter was calculated in comparison to the ground pressure of 1,013 hPa.

Table 2. Meteorological conditions for air sampling on August 1, 1992

	altitude				
	1.5m	5m	30m	50m	100m
sampling time	12:00-12:45	12:00-12:45	10:00-10:20	10:30-10:50	11:10-11:30
weather*	cloudy	cloudy	cloudy	cloudy	fine
temperature (°C)*	32	32	31	31	33
wind direction*	E	E	NE	NE	NNE
wind speed (m/sec)*	1.0	1.0	1.0	1.5	1.5
pressure(hPa)**	1013	1012	1009	1007	1001

* : Meteorological conditions were observed at 1.5 m in height.

**: The pressure of each altitude was calculated in comparison to pressure as 1,013 hPa at 1.5 m in height.

and rotor diameter 3.1 m). About 100 L volumes of air at 30 m, 50 m and 100 m in height were sampled with these silica gel columns at the rate of 1.2 L/min in a flight for 20 minutes over point "A". The altitude of radio-controlled helicopter was monitored and controlled by an altimeter.

Air was sampled at 150 m, 300 m, 500 m and 800 m in height by the helicopter (AeroSpacial AS-350) with 192 km/hr of speed along each side of the triangle shown in Fig. 1 (a). Two sets of silica gel columns and pumps (Shibata Mini-pump MP-50NC) were loaded in the pilot-boarding helicopter, and 100 L of air at outdoor of the helicopter was sampled with silica gel columns at the rate of 1-2 L/min during a flight at 150-800 m in height over Southwest of Ibaraki Prefecture on March 19 and July 23, 1991.

Meteorological conditions such as weather and air temperature on March 19, 1991 were measured at 1.5 m in height on the surface of ground at the heliport

(Kawagoe, Saitama Pref.). The weather was fine, and the temperature was 10°C at 12:30 and 7°C at 14:00. The weather, air temperature, wind direction, wind speed and the visibility on July 23, 1991 were measured during a flight at sampling altitudes. The pressure at each altitude was calculated from ICAO Standard in comparison to the ground pressure of 1,013 hPa. These meteorological conditions and the time of air sampling are shown in Tab. 1. It was observed that the aerosol layer was floating only at 500 m in height on July 23, 1991, and also the visibility at 500 m was not good.

The meteorological conditions (weather, temperature, humidity, wind direction and wind speed) on August 1, 1992 were measured at point "A", and these conditions and the time of air sampling are shown in Tab. 2. All conditions were observed at 1.5 m in height.

Trapped components in a silica gel column were eluted with 10 mL of acetone. 1 mL of 1% DEG/acetone solution was added to the extracted solution for only the sample in 1991. This acetone solution was concentrated by evaporation with a rotary evaporator in a water bath at <30°C under a reduced pressure, dried by N_2 gas, and then filled up to 1 mL with acetone. The concentrations of DAPs were determined with GC/MS (SIM), which was set to the condition of GC given in Tab. 3. The retention times and the M/Z values of a few representative peaks in SIM were 8.55 min, 163 and 194 for DMP; 10.70 min, 149 and 177 for DEP; 11.85 min, 149 and 209 for DiPP; 13.30 min, 149 and 189 for DALP; 13.85 min, 149 and 209 for DnPP; 15.65 min, 149 and 223 for DiBP; 17.35 min, 149 and 205 for DnBP; 19.40 min, 149 and 237 for DnAP; 24.10 min, 149 and 206 for BBP; 25.50 min, 129 and 147 for DOA; 26.90 min, 149, 167 and 249 for DCHP; 27.70

Table 3. Gas chromatographic conditions for DAPs analysis

GC/MS	Shimadzu QP-5050
Column	J&W Scientific, capillary DB-1, id 0.25mm×length 30m, film thickness 0.25 μm
Column temperature	60°C held for 1 min; heating at 40°C/min, 170°C held for 0.1 min; heating at 10°C/min, 250°C held for 7 min; heating at 20°C/min, 270°C held for 10 min
Injector	splitless
Injection temperature	280°C
Interface temperature	280°C
Carrier gas	He, 100 kPa, constant flow control
Flow rate	2.0 mL/min (total), 1.6 mL/min (in column)
Line speed	46.4 cm/sec
Sample size	1 μL
Ion source	EI
SIM sampling rate	0.05 sec
Ion multi. volt	1.0-1.5 kV

min, 149 and 167 for DEHP; 29.40 min, 149, 167 and 293 for DNP, respectively, where the abbreviated names of DAPs are listed in Tab. 4. The standard solutions of DAPs were diluted with acetone to the concentrations of 0.01, 0.1, 1 and 10 mg/L. From the results that DAPs except DEHP and DnBP had linear responses between 0.01 and 10 mg/L and a sampling volume of air was 100 L, the detection limit of them would be calculated to be 0.1 μg/cu m. However, both DEHP and DnBP had linear responses between 0.1 and 10 mg/L, thus the detection limit of DEHP and DnBP were 1 μg/cu m. The concentration (C: μg/cu m) at 20°C and 1,013 hPa was calculated from the following equation (1).

$$C=(W-Wo)/V\times(273+t)/(273+20)\times1013/P \qquad (1)$$

Here, W (μg) was a weight of trapped chemical, Wo (μg) was a blank weight in columns, V (cu m) was a sampling volume of air, t (°C) was a temperature at a sampling altitude and P (hPa) was a pressure at a sampling altitude.

RESULTS AND DISCUSSION

Recoveries on DAPs from a silica gel column were ranged from 88% to 106% (average: 96%), when 10 μg of DAPs were fortified and then they were eluted with 10 mL of acetone. The collection efficiencies (C.E.) of volatilized DAPs

Table 4. Recoveries using silica gel and blanks of DAPs

chemicals	recovery(%)[a]		blank (μg/mL or μg/column)			
	SILICA[b]	C.E.[b]	ACE(PR)	ACE(GR)	HEX(PR)	COL[c]
Phthalates						
benzyl butyl(BBP)	98.9±6.9	76.2±8.0	0.002	0.002	0.002	0.016
diallyl (DALP)	97.6±2.5	67.5±1.9	0.003	0.000	0.000	0.014
di-n-amyl(DnAP)	97.0±4.9	73.5±0.9	0.000	0.000	0.000	0.000
di-n-butyl(DnBP)	96.4±3.4	94.7±14.9	0.006	0.015	0.015	0.154
dicycrohexyl (DCHP)	93.7±3.9	82.1±2.9	0.002	0.002	0.001	0.003
diethyl (DEP)	90.9±5.9	76.7±5.3	0.000	0.000	0.000	0.027
di(2-ethylhexyl) (DEHP)	106.1±3.5	81.2±8.6	0.004	0.004	0.002	0.243
diisobutyl (DiBP)	95.3±3.3	85.4±14.5	0.000	0.000	0.015	0.034
diisopropyl (DiPP)	89.9±3.9	80.1±8.4	0.002	0.000	0.002	0.001
di-n-nonyl (DNP)	99.8±4.3	100.6±8.1	0.000	0.000	0.000	0.026
di-n-propyl (DnPP)	96.3±4.3	85.1±5.0	0.001	0.001	0.002	0.001
dimethyl (DMP)	88.2±5.0	70.1±5.6	0.003	0.000	0.000	0.004
Adipate						
dioctyl (DOA)	97.5±2.5	76.8±0.9	0.004	0.004	0.005	0.026
average	96.0±4.5	80.8±8.9				
total			0.027	0.028	0.029	

a) SILICA: recovery from a silica gel column, C.E.: collection efficiency.

b) Mean±standard deviation.

c) ACE: acetone, HEX: hexane, COL: SEP-PAK SILICA.

Table 5. Concentrations (μg/cu m) of DAPs in the atmosphere at high altitude

	92.8.1					91.3.19					91.7.23 [a]			
	1.5	5	30	50	100	1.5	150	300	500	800	150	300	500	800 [b]
Phthalates														
BBP	0.2	0.6	<0.1	<0.1	<0.1	0.5	<0.1	<0.1	1.2	0.6	0.3	<0.1	<0.1	<0.1
DALP	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
DnAP	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
DnBP	23	2	14	6	<1	100	14	10	17	14	10	19	79	11
DCHP	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
DEP	0.6	<0.1	<0.1	<0.1	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
DEHP	21	10	21	14	3	260	240	220	220	150	1500	87	5300	170
DiBP	<0.1	<0.1	<0.1	<0.1	<0.1	21	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
DiPP	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
DNP	0.6	0.2	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
DnPP	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
DMP	<0.1	<0.1	<0.1	<0.1	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Adipate														
DOA	1.0	<0.1	1.0	<0.1	<0.1	49	<0.1	<0.1	<0.1	<0.1	39	15	6.0	<0.1

a) Sampling date (y. m. d.).
b) Sampling altitude (m).

were ranged from 68% to 101% (average: 81%), when 10 μg of DAPs were loaded in a glass tube, then they were volatilized by passing of 500-1000 L of air and finally they were trapped into a silica gel column. C.E. was calculated by equation (2).

$$\begin{aligned}\text{C.E.} &= (\text{trapped wt.}) / [(\text{loaded wt. in a glass tube})-(\text{remained wt. in a glass tube})]\times 100\\ &= (\text{trapped weight}) / (\text{volatilized weight})\times 100 \qquad (2)\end{aligned}$$

Since some DAPs are used for a plasticizer, it was possible that these DAPs were contaminated into organic solvents through the atmosphere of laboratory. The blank levels of DAPs in the solvents were determined when 0.1 mg/L of standard

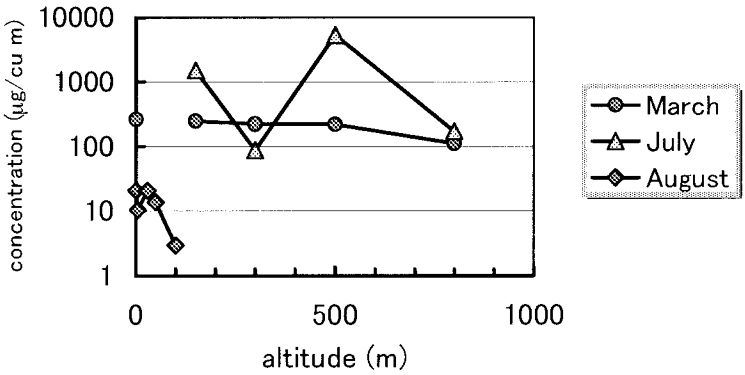


Figure 2. Concentration dependence of di(2-ethylhexyl) phthalate (DEHP) on altitudes

solution was used (Tab. 4). Acetone (PR) was used for the solvent because of the lowest blank concentration. The blanks (Wo) of DAPs in a silica gel column as an adsorbent were measured (Tab. 4).

The concentrations of DAPs at high altitude are shown in Table 5. DALP, DnAP, DCHP, DiPP and DnPP were not detected in all samples. DMP, DEP and DiBP were detected only on the surface of ground. The concentrations of BBP, DnBP, DEHP and DOA on both March 1991 and August 1992 were decreased generally with altitude. The concentrations of DEHP at high altitude are shown in Fig. 2. On July 23, 1991, the concentrations of DnBP and DEHP were maximum at 500 m in height. And also, it was observed that the aerosol layer floated about 500 m in height. The presence of an inverse layer was estimated about 500 m in height on July 23, 1991, because the temperature at 500 m in height was higher than those at other altitudes and the visibility at 500 m was not good (Tab. 1). Therefore, the lid of the inverse layer suppressed the diffusion of the atmosphere from the ground to the higher sky, thus the concentrations of chemicals at 500 m in height were obviously increased.

The concentrations of DAPs in July were higher than those in March at the same altitude because the temperature in July was higher than in March. It was reported that the concentrations in summer or at urban sites were higher than those in winter or at rural sites (Environment Agency of Japan 1986). The maximum concentrations of DAPs had the order as DEHP > DnBP > DOA > DiBP > BBP = DNP = DEP > DMP. While there was no correlation between the maximum values and the vapor pressure or the boiling point, these maximum concentrations of DAPs had a positive correlation with producing amounts of DAPs in 1984 or 1988 (The Chemical Daily Co., Ltd. 1986, 1990 shown in Fig. 3 (R^2=0.96). It was noticed that the concentrations of DEHP and DnBP at 1.5 m in height were higher than the reported concentrations. Silica gel was used to trap chemicals in this report, although polyurethane foam (PUF) (Atlas et al. 1981; Yamasaki et al. 1977) and Tenax GC (Environmental Agency of Japan 1986) had

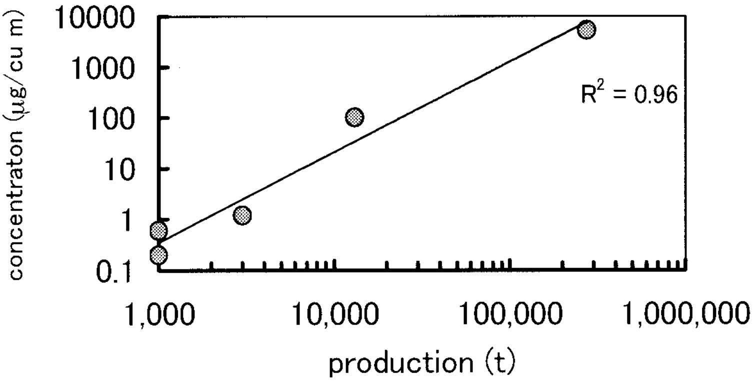


Figure 3. Correlation between maximum concentrations (●) and producing amounts of DAPs

been used in the previous study. It was estimated that many DAPs were dissolved into the moisture in the air and this moisture was trapped with silica gel; *i.e.* silica gel could trap gaseous and aqueous components and particulate matter. However, the moisture was difficult to be trapped with PUF or Tenax; *i.e.* PUF or Tenax could trap only gaseous components and particulate matter.

The collection efficiencies of DAPs were over 70%, using silica gel cartridge column as an adsorbent. A number of DAPs were detected in the atmosphere at high altitude, although pesticides were not detected in the atmosphere at over 150 m altitude. It was concluded that the use of a helicopter was adequate to sample the air at high altitude. And silica gel was one of the suitable adsorbents to trap pesticides, however this was not suitable for trapping DAPs because of the contamination from blanks.

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