

## Calibration and Field survey of Passive Air Samplers for Persistent Organic Pollutants

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### Abstract

Commonly, the high volume air sampler or low volume air sampler is the most widely used for sampling POPs in ambient air. These methods need pump which requires costly sampling equipment and a source of electricity, so it is not feasible for conducting sampling everywhere. Therefore more feasible approach that was employed here was to use passive air samplers (PAS). PAS consists of polyurethane foam (PUF) covered with a stainless steel chamber to investigate gas-phase concentration of polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs). PAS and low-volume air sampler were deployed for about two months simultaneously from July to August 2009 and from December 2009 to January 2010 in Kobe. Data obtained using passive air sampler (PAS) was compared to active low volume air sampling data in order to estimate the sampling rate, verify the effectiveness from the point of view of isomer patterns.

### Introduction

Passive air sampler (PAS) is very superior for monitoring long-term trends, which can enable the cost-effective collection of monthly or seasonally integrated air samples. PAS are chemical accumulators that rely on air currents to deliver chemical to the adsorbent materials. POPs diffuse into the sampling media during exposure and integrate the air concentrations over the sampling period. The PUF-based PAS is probably the most widely used because they are easy to prepare, extract and handle, and inexpensive. In this study, the uptake of POPs by PUF-based PAS we developed was characterized which allows air concentrations to be determined and all isomers of PCBs were analyzed. Here target compounds are PCB, HCH, HCB, chlordane, nonachlor, mirex. PCB had been widely used until 1972 in Japan as mainly electric appliances, heat exchange fluids, carbonless paper, capacitors of the fluorescent lights and the amount of PCBs produced during 1954 and 1971 is 58000 tons in Japan. PCBs consist of 209 differently chlorinated congeners. PCBs product produced by Kaneka Chemical, KC-300, KC-400, KC-500, KC-600 were of different congeneric proportions and purposes. Principal isomers differ among PCB products. For this reason, we have been tried to analyze all isomers of PCBs using HRGC/HRMS. The final target of this study is to investigate air concentrations and patterns of PCBs by PAS. Hexachlorocyclohexane (HCH) is a manufactured chemical that exists in eight chemical forms called isomers. Technical HCH is pesticide consisting if a mixture of five stable isomers which have been shown to have serious short- and long-term health effects; the isomers are • •60-70%, • •10-12%, • •6-10%, • •3-4% and • •3-4%. HCB is a fungicide formerly used as a seed treatment, especially on wheat to control the fungal •• disease bunt. It is also a by-product of the manufacture of industrial chemicals including

carbon tetrachloride, perchlorethylene, trichloroethylene and pentachlorobenzene. It is also a known impurity in several pesticide formulations, as well as can be present in those processes that generates dioxins and furans. Technical chlordane was the mixture of more than 140 compounds, and was mainly used for termite control in Japan from 1950. In 1968 it was banned for agriculture, however used for termite control, until the Chemical Substances Control Law restricted it in 1986. This mixture is complex including 40% of octachlorinated isomers, 20% of nonachlorinated isomers, 4.8% of heptachlorinated isomers, and 7.3% of hexachlorinated isomers.

## Materials and Method

### Passive Air Sampler (PAS) and Active Air Sampler (AAS)

PAS consist of an accumulating/adsorbing medium that has a high retention capacity for the target analytes. We followed the theory of uptake of POPs by PUF disks described in the paper.<sup>1</sup> A PUF disk is supported on a metal rod in a central position between the upper and lower bowls which is made of two stainless steel to buffer the air flow to the disk and to shield it from precipitation and light. There were two objects to the investigation. Objective 1 was to calibrate the samplers against the conventional AAS, to derive the information on field based uptake rate by collecting samplers after different exposure times. Eight PAS were deployed simultaneously to derive the uptake rate from July to August 2009. These samplers were collected in series one-by-one every week. Weekly low volume air samplers were also taken at the same site. Polyurethane foams (PUF ; 9cm diameter ; 5cm thick ; surface area 268cm<sup>2</sup> ; mass 5.5g ; volume 318cm<sup>3</sup> ; density 0.017g/cm<sup>3</sup>) were pre-cleaned by acetone solvent using soxlet extraction. The low volume air sampler mounts quartz micro fiber (QMF, 150mm in diameter) and three same polyurethane foams with sample amount being approximately 1000m<sup>3</sup> and the flow rate 100L/min. Objective 2 was to compare the results derived from the different shape of PUF, thick and thin type. Thick type is the noted above PUF. Thin type PUF is 9cm diameter ; 1cm thick ; surface area 155cm<sup>2</sup> ; mass 1.5g ; volume 64cm<sup>3</sup> ; density 0.024g/cm<sup>3</sup>. These PAS were deployed simultaneously for 8 weeks from December 2009 to January 2010. The samples were analyzed by high resolution gas chromatography device(HP 6890)/ a high resolution mass spectrometer(JEOL Ltd.JMS-800D).

## Results and discussions

### Uptake rate study

Theoretically, an uptake profile for POPs to PUF can be divided into 3 sections; a linear uptake phase, a curvilinear uptake phase and equilibrium partitioning. During the linear state, sampling ( or uptake ) rates ( m<sup>3</sup>/day ) can be calculated from the concentration of analytes in the PUF ( pg ), normalized to the exposure time ( day ), divided by the average concentration of analytes in the air over the sampling

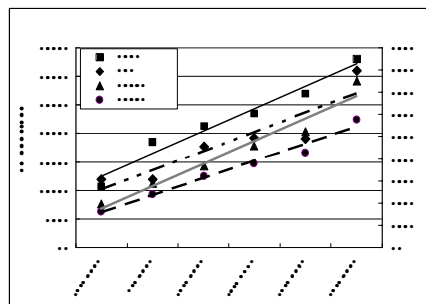


Fig 1 Adsorbed amount to PAS

••(#28: primary axis, #3,#118,#153: secondary axis)

period (pg/m<sup>3</sup>) obtained by the low volume air sampler. The accumulated PCB amount generally increased linearly in the PAS over time during the sampling period as examples.(Fig.1) The adsorbed amount to PAS of other isomers also increases up to two months in this experiment. In this study period, target compounds don't reach equilibrium, suggesting that PAS have a capacity to continue linear uptake beyond 2 months tested here. So this time period is considered to be in the linear stage and sampling rate (SR) can be calculated according to the aforementioned theory. SR for each PCBs homologue (mono to octa ), total PCB and POPs are shown in Table1.

.... Table 1 SR.(sampling rate) for PCBs and selected POPs ....

Compound	SR (Sampling Rate)
PCB-28	0.0001
PCB-52	0.0002
PCB-101	0.0003
PCB-153	0.0004
PCB-180	0.0005
PCB-209	0.0006
PCB-203	0.0007
PCB-207	0.0008
PCB-219	0.0009
PCB-223	0.0010
PCB-229	0.0011
PCB-237	0.0012
PCB-247	0.0013
PCB-253	0.0014
PCB-267	0.0015
PCB-277	0.0016
PCB-283	0.0017
PCB-297	0.0018
PCB-303	0.0019
PCB-317	0.0020
PCB-323	0.0021
PCB-337	0.0022
PCB-343	0.0023
PCB-357	0.0024
PCB-363	0.0025
PCB-377	0.0026
PCB-383	0.0027
PCB-397	0.0028
PCB-403	0.0029
PCB-417	0.0030
PCB-423	0.0031
PCB-437	0.0032
PCB-443	0.0033
PCB-457	0.0034
PCB-463	0.0035
PCB-477	0.0036
PCB-483	0.0037
PCB-497	0.0038
PCB-503	0.0039
PCB-517	0.0040
PCB-523	0.0041
PCB-537	0.0042
PCB-543	0.0043
PCB-557	0.0044
PCB-563	0.0045
PCB-577	0.0046
PCB-583	0.0047
PCB-597	0.0048
PCB-603	0.0049
PCB-617	0.0050
PCB-623	0.0051
PCB-637	0.0052
PCB-643	0.0053
PCB-657	0.0054
PCB-663	0.0055
PCB-677	0.0056
PCB-683	0.0057
PCB-697	0.0058
PCB-703	0.0059
PCB-717	0.0060
PCB-723	0.0061
PCB-737	0.0062
PCB-743	0.0063
PCB-757	0.0064
PCB-763	0.0065
PCB-777	0.0066
PCB-783	0.0067
PCB-797	0.0068
PCB-803	0.0069
PCB-817	0.0070
PCB-823	0.0071
PCB-837	0.0072
PCB-843	0.0073
PCB-857	0.0074
PCB-863	0.0075
PCB-877	0.0076
PCB-883	0.0077
PCB-897	0.0078
PCB-903	0.0079
PCB-917	0.0080
PCB-923	0.0081
PCB-937	0.0082
PCB-943	0.0083
PCB-957	0.0084
PCB-963	0.0085
PCB-977	0.0086
PCB-983	0.0087
PCB-997	0.0088
PCB-1003	0.0089
PCB-1017	0.0090
PCB-1023	0.0091
PCB-1037	0.0092
PCB-1043	0.0093
PCB-1057	0.0094
PCB-1063	0.0095
PCB-1077	0.0096
PCB-1083	0.0097
PCB-1097	0.0098
PCB-1103	0.0099
PCB-1117	0.0100
PCB-1123	0.0101
PCB-1137	0.0102
PCB-1143	0.0103
PCB-1157	0.0104
PCB-1163	0.0105
PCB-1177	0.0106
PCB-1183	0.0107
PCB-1197	0.0108
PCB-1203	0.0109
PCB-1217	0.0110
PCB-1223	0.0111
PCB-1237	0.0112
PCB-1243	0.0113
PCB-1257	0.0114
PCB-1263	0.0115
PCB-1277	0.0116
PCB-1283	0.0117
PCB-1297	0.0118
PCB-1303	0.0119
PCB-1317	0.0120
PCB-1323	0.0121
PCB-1337	0.0122
PCB-1343	0.0123
PCB-1357	0.0124
PCB-1363	0.0125
PCB-1377	0.0126
PCB-1383	0.0127
PCB-1397	0.0128
PCB-1403	0.0129
PCB-1417	0.0130
PCB-1423	0.0131
PCB-1437	0.0132
PCB-1443	0.0133
PCB-1457	0.0134
PCB-1463	0.0135
PCB-1477	0.0136
PCB-1483	0.0137
PCB-1497	0.0138
PCB-1503	0.0139
PCB-1517	0.0140
PCB-1523	0.0141
PCB-1537	0.0142
PCB-1543	0.0143
PCB-1557	0.0144
PCB-1563	0.0145
PCB-1577	0.0146
PCB-1583	0.0147
PCB-1597	0.0148
PCB-1603	0.0149
PCB-1617	0.0150
PCB-1623	0.0151
PCB-1637	0.0152
PCB-1643	0.0153
PCB-1657	0.0154
PCB-1663	0.0155
PCB-1677	0.0156
PCB-1683	0.0157
PCB-1697	0.0158
PCB-1703	0.0159
PCB-1717	0.0160
PCB-1723	0.0161
PCB-1737	0.0162
PCB-1743	0.0163
PCB-1757	0.0164
PCB-1763	0.0165
PCB-1777	0.0166
PCB-1783	0.0167
PCB-1797	0.0168
PCB-1803	0.0169
PCB-1817	0.0170
PCB-1823	0.0171
PCB-1837	0.0172
PCB-1843	0.0173
PCB-1857	0.0174
PCB-1863	0.0175
PCB-1877	0.0176
PCB-1883	0.0177
PCB-1897	0.0178
PCB-1903	0.0179
PCB-1917	0.0180
PCB-1923	0.0181
PCB-1937	0.0182
PCB-1943	0.0183
PCB-1957	0.0184
PCB-1963	0.0185
PCB-1977	0.0186
PCB-1983	0.0187
PCB-1997	0.0188
PCB-2003	0.0189
PCB-2017	0.0190
PCB-2023	0.0191
PCB-2037	0.0192
PCB-2043	0.0193
PCB-2057	0.0194
PCB-2063	0.0195
PCB-2077	0.0196
PCB-2083	0.0197
PCB-2097	0.0198
PCB-2103	0.0199
PCB-2117	0.0200
PCB-2123	0.0201
PCB-2137	0.0202
PCB-2143	0.0203
PCB-2157	0.0204
PCB-2163	0.0205
PCB-2177	0.0206
PCB-2183	0.0207
PCB-2197	0.0208
PCB-2203	0.0209
PCB-2217	0.0210
PCB-2223	0.0211
PCB-2237	0.0212
PCB-2243	0.0213
PCB-2257	0.0214
PCB-2263	0.0215
PCB-2277	0.0216
PCB-2283	0.0217
PCB-2297	0.0218
PCB-2303	0.0219
PCB-2317	0.0220
PCB-2323	0.0221
PCB-2337	0.0222
PCB-2343	0.0223
PCB-2357	0.0224
PCB-2363	0.0225
PCB-2377	0.0226
PCB-2383	0.0227
PCB-2397	0.0228
PCB-2403	0.0229
PCB-2417	0.0230
PCB-2423	0.0231
PCB-2437	0.0232
PCB-2443	0.0233
PCB-2457	0.0234
PCB-2463	0.0235
PCB-2477	0.0236
PCB-2483	0.0237
PCB-2497	0.0238
PCB-2503	0.0239
PCB-2517	0.0240
PCB-2523	0.0241
PCB-2537	0.0242
PCB-2543	0.0243
PCB-2557	0.0244
PCB-2563	0.0245
PCB-2577	0.0246
PCB-2583	0.0247
PCB-2597	0.0248
PCB-2603	0.0249
PCB-2617	0.0250
PCB-2623	0.0251
PCB-2637	0.0252
PCB-2643	0.0253
PCB-2657	0.0254
PCB-2663	0.0255
PCB-2677	0.0256
PCB-2683	0.0257
PCB-2697	0.0258
PCB-2703	0.0259
PCB-2717	0.0260
PCB-2723	0.0261
PCB-2737	0.0262
PCB-2743	0.0263
PCB-2757	0.0264
PCB-2763	0.0265
PCB-2777	0.0266
PCB-2783	0.0267
PCB-2797	0.0268
PCB-2803	0.0269
PCB-2817	0.0270
PCB-2823	0.0271
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PCB-2843	0.0273
PCB-2857	0.0274
PCB-2863	0.0275
PCB-2877	0.0276
PCB-2883	0.0277
PCB-2897	0.0278
PCB-2903	0.0279
PCB-2917	0.0280
PCB-2923	0.0281
PCB-2937	0.0282
PCB-2943	0.0283
PCB-2957	0.0284
PCB-2963	0.0285
PCB-2977	0.0286
PCB-2983	0.0287
PCB-2997	0.0288
PCB-3003	0.0289
PCB-3017	0.0290
PCB-3023	0.0291
PCB-3037	0.0292
PCB-3043	0.0293
PCB-3057	0.0294
PCB-3063	0.0295
PCB-3077	0.0296
PCB-3083	0.0297
PCB-3097	0.0298
PCB-3103	0.0299
PCB-3117	0.0300
PCB-3123	0.0301
PCB-3137	0.0302
PCB-3143	0.0303
PCB-3157	0.0304
PCB-3163	0.0305
PCB-3177	0.0306
PCB-3183	0.0307
PCB-3197	0.0308
PCB-3203	0.0309
PCB-3217	0.0310
PCB-3223	0.0311
PCB-3237	0.0312
PCB-3243	0.0313
PCB-3257	0.0314
PCB-3263	0.0315
PCB-3277	0.0316
PCB-3283	0.0317
PCB-3297	0.0318
PCB-3303	0.0319
PCB-3317	0.0320
PCB-3323	0.0321
PCB-3337	0.0322
PCB-3343	0.0323
PCB-3357	0.0324
PCB-3363	0.0325
PCB-3377	0.0326
PCB-3383	0.0327
PCB-3397	0.0328
PCB-3403	0.0329
PCB-3417	0.0330
PCB-3423	0.0331
PCB-3437	0.0332
PCB-3443	0.0333
PCB-3457	0.0334
PCB-3463	0.0335
PCB-3477	0.0336
PCB-3483	0.0337
PCB-3497	0.0338
PCB-3503	0.0339
PCB-3517	0.0340
PCB-3523	0.0341
PCB-3537	0.0342
PCB-3543	0.0343
PCB-3557	0.0344
PCB-3563	0.0345
PCB-3577	0.0346
PCB-3583	0.0347
PCB-3597	0.0348
PCB-3603	0.0349
PCB-3617	0.0350
PCB-3623	0.0351
PCB-3637	0.0352
PCB-3643	0.0353
PCB-3657	0.0354
PCB-3663	0.0355
PCB-3677	0.0356
PCB-3683	0.0357
PCB-3697	0.0358
PCB-3703	0.0359
PCB-3717	0.0360
PCB-3723	0.0361
PCB-3737	0.0362
PCB-3743	0.0363
PCB-3757	0.0364
PCB-3763	0.0365
PCB-3777	0.0366
PCB-3783	0.0367
PCB-3797	0.0368
PCB-3803	0.0369
PCB-3817	0.0370
PCB-3823	0.0371
PCB-3837	0.0372
PCB-3843	0.0373
PCB-3857	0.0374
PCB-3863	0.0375
PCB-3877	0.0376
PCB-3883	0.0377
PCB-3897	0.0378
PCB-3903	0.0379
PCB-3917	0.0380
PCB-3923	0.0381
PCB-	

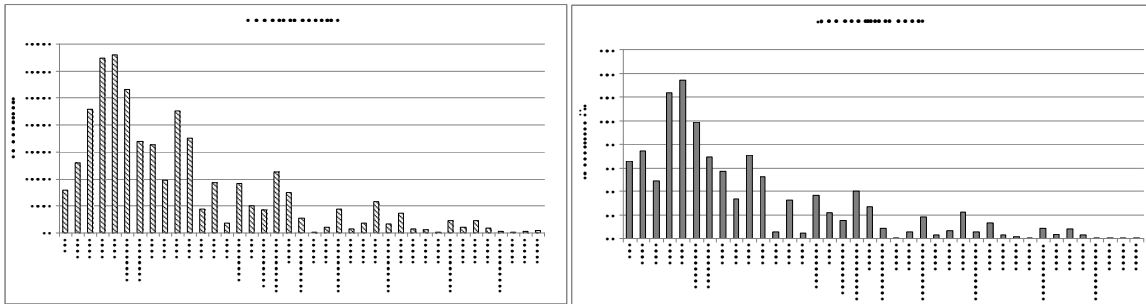


Fig3 congener pattern comparison

### PUF shape comparison study

Thick and thin type PUF were compared by deploying simultaneously at urban site in winter. Thick type had more adsorption capacity (in aspect of adsorbed amount) than thin type in proportion to surface area. And when normalized to surface area, SR was the almost same value. And that is for example SR for #118 is 5.7m<sup>3</sup>/day, 3.8 m<sup>3</sup>/day and normalized values are 0.021 m<sup>3</sup>/day/cm<sup>2</sup>, 0.024 m<sup>3</sup>/day/cm<sup>2</sup> respectively. This result shows that thick type PUF has more ability to detect low-level concentrations than thin type.

### Location study

In a separate study PAS were deployed for about 2 months at 2 points (urban, rural area). Sequestered concentrations and the aforementioned sampling rates were used to calculate atmospheric concentrations. Table 3 shows the concentration level of POPs in urban and rural area seasonally. The results seem to show a good agreement with the concentration level of the other survey by ASS. The ratio  $\alpha/\gamma$ -HCH with concentrations of each isomer are useful source indicators. Also this ratio is an indicator of the current use of technical HCH. In this study  $\alpha/\gamma$  ratio was 1.5 • • 3.6. This is the reason that these results reflect the usage in Japan where the most part of HCH is • • isomer (on the contrary Linden, • • isomer ratio of HCH is over 99%, had been used in China.) Much more data by PAS should be accumulated seasonally at many points to illustrate a phenomenon of these.

Table 3 Concentration level by PAS at urban and rural site (pg/m<sup>3</sup>)

	****	*****	*****	*****	*****	*****	*****	*****
*****	***	***	***	***	***	***	***	***
*****	***	**	***	***	***	**	***	***
*****	***	**	***	***	**	**	***	**
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*****	***	***	***	***	***	***	***	***
*****	***	***	***	***	***	***	***	***
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*****	***	***	***	***	***	***	***	***
*****	***	***	***	***	***	***	***	***
*****	***	***	***	***	***	***	***	***
*****	***	***	***	***	***	***	***	***
*****	***	***	***	***	***	***	***	***
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### Acknowledgement

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