FREQUENT MONITORING OF PERSISTENT ORGANOCHLORINE PESTICIDES IN BACKGROUND AIR AT TAM DAO MOUNTAIN (VIETNAM)

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Introduction

Persistent Organochlorine pesticides (OCPs) are typical persistent organic pollutants (POP). They are very persistent in environment and highly bioaccumulated in food chains and can cause damages to environment, wildlife as well as human health[1]. In accordance with requirement of the Stockholm Convention, OCPs have been banned and eliminated from their applications in many countries. Since the Stockholm Convention took effect, significant efforts have been made globally to control and reduce their releases into environment. As the result, reduction of OCPs level in various environmental media has been suggested in Europe, North America and Arctic region. It is important to note that Article number sixteen of the Stockholm Convention particularly emphasizes on requirement of effectiveness evaluation for the implementation. Following agreement of the Conference of Parties 4 (COP 4) in May 2009, a hoc working group was established for the effectiveness evaluation and the first announcement was released in November 2009. Several gaps were identified in the report and among those, sufficient monitoring data is important factor for comprehensive assessment. The group also agreed that the second evaluation term will be done in 2013 and thus comprehensive monitoring data is very much necessary for adequate evaluation.

In fact, high frequent sampling programs for monitoring of POPs in air have been carried out in Japan and Korea (known as supersite monitoring programs)[2] for archiving data of the East Asian region. Even though such monitoring data has been proved as useful tool for the evaluation, it has never been carried out in South East Asian region, which is considered as an important source of POPs to the global environment. In order to facilitate effectiveness evaluation of the Stockholm Convention in South East Asia, Vietnam Environment Administration and Ministry of Environment Japan have jointly established a frequent POPs monitoring study in pristine area namely Tam Dao mountain, in north Vietnam. In this study, we have carried out monthly sampling of background air over twelve month period for determination of selected OCPs including HCB, Aldrin, Dieldrin, Endrin, DDTs, Chlordane compounds, Heptachlor, Mirex and Toxaphene.

Materials and methods

Air sample collection

Ambient air samples were collected in Tam-Dao Mountain every month from October 2009-November 2010. In each sampling time, three air samples were collected continuously in three days, using high volume air sampler (HV700, Shibata Co., Japan) at pumping rate of 700 L/min for 24 hours. About 1,000 m^3 of air was drawn through a 10.2 cm diameter QFF followed by a 8.0 cm diameter 7.5 cm thick of PUF plug and 8.0 cm activated carbon filter (ACF). The particle phases were mainly collected by QFFs, and gas phases were mainly collected by PUF plugs and the carbon layer. Prior to sampling, QFFs were baked at 600^0C for 6 hours to remove any organic contaminant; PUF plug and ACF were pre-cleaned by Soxhlet extraction, dried overnight in a vacuum desicator and stored in solvent-rinsed glass jars with Teflon lined lids before use. When transporting to the field, QFF, PUF and ACF were kept in metallic containers sealed by Teflon tapes. Travel blank samples were carefully prepared to control quality of the samplings. Right before sampling was taken place, ^{13}C-surrogate compounds were spiked into the PUF for controlling recovery. After sampling, QFFs were wrapped with aluminum foils and sealed with double layers of polyethylene bags, and PUF plugs were placed in solvent-rinsed glass jars with Teflon-lined lids, and then transported to the laboratory. It is necessary to note that after brought to laboratory in Vietnam, the samples were transported to our partner laboratory in Japan (Japan Environmental Sanitation

Center – JCES) for chemical analysis. Meteorological data, including temperature, air pressure, relative humidity and rainfall were recorded during sampling period.

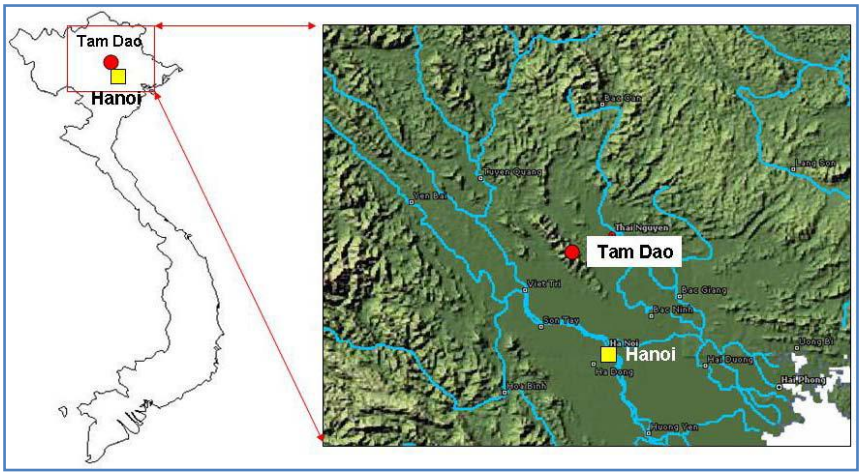


Figure 1: The Tam Dao sampling site (Vietnam) for monitoring of POPs in air

Chemical analysis

The pollutants in QFF, PUF and ACF were extracted by Soxhlet using Acetone (3 hours) and followed by Toluene (24 hours). The extracts from QFFs, PUFs and ACFs were combined together for further clean-up by Florisil column. The first fraction was eluted by mixture of DCM/Hexane (20/80) and the second one was eluted by DCM. Two fractions were concentrated by rotary vacuum, syringe spike compound was added and the solution was further blown down to 100 uL by Nitrogen stream. Except of Toxaphenes, all OCPs were analyzed by High Resolution Gas Chromatography coupled with High Resolution Mass Spectrometer (HRGC/HRMS; HRMS is AutoSpec Ultima NT produced by Waters Company). HRMS was operated in SIM mode with resolution >10,000. Toxaphene compounds were analyzed by High Resolution Gas Chromatography coupled with Low Resolution Mass Spectrometer (HRGC/LRMS; Agilent 7890) operated in Negative Chemical Ionization using Isobutan.

Results and discussion

Level of OCPs in air at Tam Dao

Table 1 showed details of OCPs concentration in Tam Dao air over a twelve-month period (October 2009 – October 2010). Among the monitored pollutants, HCB has the highest level ranging from 98-387 pg/m^3, followed by DDTs (16-49 pg/m^3) and Chlordanes (1.0-4.9 pg/m^3). Other pollutants such as Aldrin, Endrin, Dieldrin and Toxaphene were not frequently detected in air samples. Method quantification limits for each compound varied among samples, normally 0.03 pg/m^3 for Aldrin, 0.2 03 pg/m^3 for Dieldrin, 0.04 03 pg/m^3 for Endrin, 0.04 03 pg/m^3 for Nonachlor, 0.07 03 pg/m^3 for Heptachlorepoxide and 0.503 pg/m^3 for Toxaphene (Planar 50 and 62).

In Figure 2, it is observed that concentration of HCB was also more variable than DDTs and Chlordanes, showing the higher levels October to April and the lower ones from May to August, which is rainy period in the north of Vietnam. This phenomenon was not observed for DDTs and Chlordanes. Perhaps weathering conditions has influenced more on HCB because of its high volatility. DDTs concentration showed less variation (11-43 pg/m3) and no trend over the whole period, suggesting that their sources are relatively stable. Chlodanes also had low levels and less variation throughout twelve months of sampling. This finding may suggest that contamination by Chlordanes is insignificant in the region and that the levels found in Tam Dao is representative for the background level.

Table 1: Three-day averaged concentration of OCPs (pg/m^3) in background air at Tam Dao Mountain

Chemicals	Oct.'09	Nov.'09	Dec.'09	Jan.'10	Feb.'10	Mar.'10	Apr.'10	May.'10	Jun.'10	Jul.'10	Aug.'10	Sept.'10	Oct.'10	Mean	Min	Max
HCB	387	157	213	170	98	207	304	105	66	66	87	220	340	186	66	387
Aldrin	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	-	-	-
Dieldrin	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	-	-	-
Endrin	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	-	-	-
p,p'-DDT	4.33	6.33	5.00	5.00	20.00	7.63	8.09	9.18	11.00	9.00	6.00	9.00	2.00	7.89	2.00	20
p,p'-DDE	4.67	4.67	6.00	6.33	7.30	6.67	6.94	8.00	9.70	8.50	6.00	9.80	5.40	6.92	4.67	9.80
p,p'-DDD	0.40	0.70	0.60	0.70	0.97	0.66	0.67	1.09	1.20	1.10	0.70	0.90	0.20	0.76	0.20	1.20
o,p'-DDT	4.27	3.53	3.10	3.93	12.57	3.83	6.88	6.06	6.00	6.00	3.00	5.00	2.00	5.09	2.00	12.57
o,p'-DDE	1.80	1.03	1.27	1.27	1.33	1.20	1.57	1.21	1.30	1.00	0.70	1.50	1.40	1.28	0.70	1.80
o,p'-DDD	0.50	0.68	0.66	0.76	0.81	0.61	0.79	1.08	1.20	1.00	0.68	0.93	0.25	0.77	0.25	1.20
trans-Chlordane	1.60	0.20	0.27	0.87	0.31	0.36	1.00	1.06	0.26	0.40	0.53	0.46	0.83	0.63	0.20	1.60
cis-Chlordane	1.67	0.57	0.50	0.97	0.39	0.44	1.02	1.11	0.41	0.55	0.80	0.63	0.95	0.77	0.39	1.67
trans-Nonachlor	0.64	0.19	0.21	0.44	0.20	0.27	0.48	0.60	0.25	0.32	0.43	0.31	0.62	0.38	0.19	0.64
cis-Nonachlor	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	-	-	-
Oxychlordane	0.27	0.20	0.14	0.14	0.14	0.10	0.16	0.15	0.14	0.14	0.14	0.21	0.21	0.17	0.10	0.27
Heptachlor	0.40	0.12	0.09	0.37	0.37	0.18	0.39	1.08	0.45	0.28	0.25	0.37	0.18	0.35	0.09	1.08
trans-Heptaepoxi	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	-	-	-
cis-Heptaepoxi	0.37	0.25	0.19	0.25	0.16	0.18	0.21	0.23	0.21	0.23	0.26	0.22	0.32	0.24	0.16	0.37
Mirex	0.76	0.33	0.24	0.39	0.16	0.20	0.35	0.43	0.19	0.25	0.35	0.47	0.47	0.35	0.16	0.76
Toxaphene (26)	0.17	0.15	0.13	0.19	0.12	0.12	0.08	0.07	0.07	0.17	0.18	0.12	43.00	0.13	0.07	0.19
Toxaphene (50)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	-	-	-
Toxaphene (62)	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	-	-	-
op'-DDT/pp'-DDT	0.98	0.56	0.62	0.79	0.63	0.50	0.85	0.66	0.55	0.67	0.50	0.56	1.00	0.65	1.00	0.63
DDT/(DDE+DDD)	0.86	1.18	0.76	0.71	2.42	1.04	1.06	1.01	1.01	0.94	0.90	0.84	0.36	1.03	0.41	1.82

ND: Not detected or not calculated due to level close to method quantification limits (refore text for more details)
Each month, three samples were collected in three continuous days and avearage conc presented here

In global comparison of HCB concentration in air, uniform distribution of HCB was found in South Korea (14–95 pg/m3), Japan (26–136 pg/m3) and Europe (1.4–8.9 pg/m3)[3,4]. However, In China, level of HCB varied largely, depending on specific locations. For example, HCB ranging from 36.6-669 pg/m^3 was found in Anhui province, 65-236 pg/m^3 in Hubei province, 41.1-183 pg/m^3 in Jiangsu province and 222pg/m^3 on average in Beijing Tongzhou district. Although HCB production was stopped in 2004, it is suggested that there are still existence of its sources in China such as emissions from waste dumpsites, from contaminated soils in the former HCB factories[5]. Besides, HCB in air at Mt. Everest which is considered as very destine region, was only in range of 4.8-12.6 pg/m3 with average of 8.9pg/m3. The HCB levels observed in Tam Dao is relatively high in comparison with those in Mt. Everest, Japan and Korea, and within the range observed in South China region. Our analysis of atmospheric trajectory implies that the level of HCB is somehow related with air bulk from the Northern hemisphere.

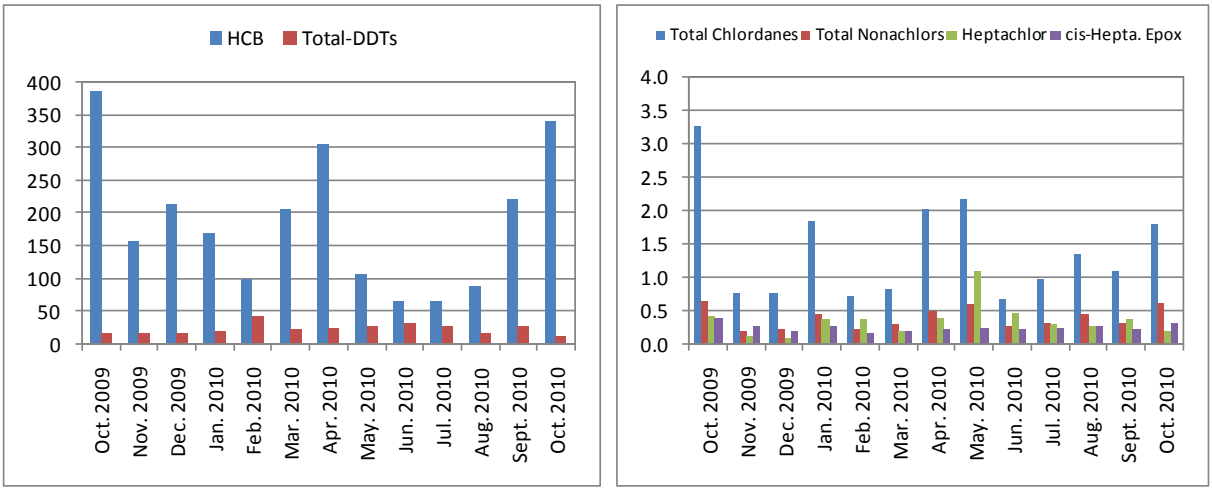


Figure 2: Variation of OCPs concentration (pg/m^3) over the twelve-month period (2009-2010)

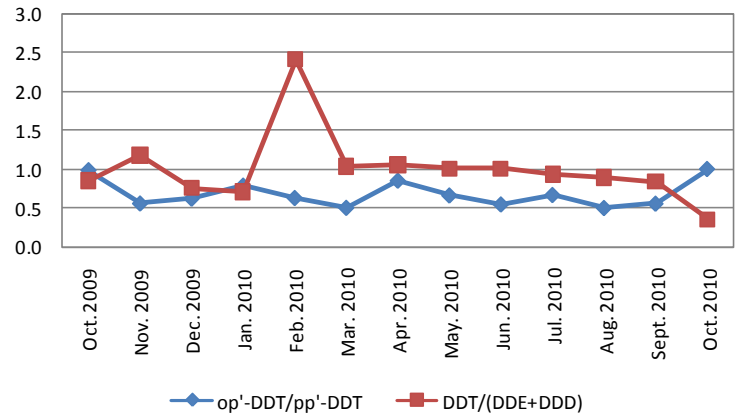
It is interesting when our data in 2010 was compared with those in previous studies carried out also at Tam Dao Mt. in 2005 and 2006[6]. However, it should be noted that two previous studies in 2005 and 2007 only collected

air samples twice a year. Nevertheless, HCB perhaps showed no trend in concentration over three sampling period (93pg/m^3 on average in 2005 and 343pg/m^3 in 2007). On the other hand, DDTs concentration in air seems to reduce over years (82.40pg/m3 on average in 2005 and 64.97pg/m3 in 2006). However, it is necessary to confirm this trend by further monitoring in future.

Composition of DDT compounds

Ratio of DDT/(DDE+DDD) is generally used as an indicator of aged DDTs. A small value of DDT/(DDE+DDD) in air is an indicative for aged DDTs while a ratio largely higher than unit may indicate recent input of fresh DDTs[7]. In this study, ratios of DDT/(DDE+DDD) were 1.01 ± 0.47 (Table 1 and Figure 3), indicating that DDTs input was not fresh. In a recent study implemented by Yang et al (2008)[8] in Guangzhou (China), the ratio of DDT/(DDE+DDD) were 1.77 ± 0.53 and 1.95 ± 0.43 at two sampling sites. The authors suggested that these ratios indicated fresh input of DDTs to air.

Figure 3: Ratio of DDTs compounds over twelve months



Ratios of *o,p'*-DDT/*p,p'*-DDT were calculated and plotted in Figure 3. It was recognized that the ratios were relatively consistent (0.68 ± 0.17; ranging between 0.5 and 1.0). In fact, this ratio is suggested to use for assessment of sources of DDTs in environment because *o,p'*-DDT is less in DDTs technical mixture but this compound is higher as impurity in a pesticide namely Difocol (Kethalne). In Guangzhou (China), *o,p'*-DDT/*p,p'*-DDT rations ranged from 1.32 to 6.51 which were significant higher than those in our study and the authors supposed that difocol is major source of o,p'-DDT to the Guangzhou environment. Nevertheless, *o,p'*-DDT/*p,p'*-DDT ratios in Tam Dao (Vietnam) were still higher than those commonly found in original technical DDTs mixtures[9]. These facts suggested that *o,p'*-DDT in Tam Dao (Vietnam) perhaps has origin from both DDTs technical mixtures as well as from difocol usage.

Acknowledgements

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