Hexachlorobutadiene (HCBD) as predominant POPs in Ambient Air : all POPs levels and trends at frequent monitoring super-sites of Japan

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Introduction: POPs are persistent in the environment and show a common property of long-range transport. Air sampling and analytical methods for this monitoring should be designed carefully to assure the quality (accuracy and precision) of the data as well having high enough sensitivity to cope with probable further decreases in environmental levels of POPs during long-term monitoring.
The POPs frequent monitoring of ambient air at the super-site Japan were started on 2009 with high sensitive analysis such as using GC-HRMS by Ministry of the Environment, Japan (MOEJ). 23 POP chemicals (groups) with the exception of dioxins and furans, the analytical methods were established and evaluated as monitoring techniques from frequent monitoring. Data on their short-term spatial variations will contribute to a clarification and understanding of environmental transport and background levels in ambient air.
HCBD monitoring was added in 2017 for new POPs.
HCBD is a halogenated aliphatic substance, mainly generated as a by-product in the manufacture of chlorinated solvents (tri- and tetrachloroethene and tetrachloromethane) or hexachlorocyclopentadiene (intermediate of cyclodiene pesticide). HCBD was used in several technical and agricultural applications and as intermediate in the chemical industry or as a product. The new POPs including HCBD
This report summarizes the HCBD trends at frequent monitoring super-sites ambient air in Japan.

Materials and Methods:
•Monitoring station; Cape Hedo in Okinawa prefecture Japan (N: 26.87, E: 128.26) OCPs levels in Cape Hedo, Okinawa, are among the lowest in the data of nation-wide POPs monitoring, supporting the view that Cape Hedo is a suitable background site for POPs monitoring in Japan.

•Sampling; 3 continuous samples/month×12month (36sample). High volume air ampler 1,000 m3 under 700 L/min, 24hrs using quarts fiber filter, Poly urethane foam (PUF) and active carbon fiber felt (ACF).

- Fortified ^{13}C surrogate $^{13}C_{12}$- PCBs mix ^{13}C-POPs mix and ^{13}C-New POPs Mix before sampling.
- Extraction: Soxhlet extraction by acetone or toluene for filter, PUF and ACF separately for target POPs.
- Comprehensive cleanup with legacy POPs and new POPs[4)].
- GC-HRMS: Autospec-Ultima (Waters/Micromass), MS resolution > 10,000 (10% Valley), DB-17HT and HT8-PCB (SGE) GC column for POPs and PCBs. GC-MS (NCI) for Toxaphene
- LC-MS/MS:API3200 (AB Sciex) for HBCD , Chlordecone and PFC
- HCBD : analytical method in ambient air was developed in 2013 by MOEJ. The brief method is: TENAX-TA 0.1L/min, 24hr (total volume 144L) TD-GC-LRMS (thermal desorption/gas chromatography mass spectrometry)
- Method validation; under MOE POPs monitoring project

Results:
Technical Point for legacy & New POPs were summarized ref 4)

Results and evaluation from frequent monitoring at supersite
Data General;
It shows similar trends of POPs levels from FY2009 to FY2016 for frequent monitoring at super site in ambient air. The concentration orders were HCBD >> HCBz, PeCBz, PCBs > PCN > HCHs > Endosulfans, Chlordanes, PFOS, PFOA, DDTs, HBCDs > Heptachlors, Dieldrin, BDE(#47). ND(not detected) :HxBB, Chlordecone. Generally clear seasonal changes, i.e. higher in summer and lower in winter, were observed in HCHs and CHLs, suggesting the dominant effect of temperature-dependent, secondary sources in these OCPs. The seasonal change

of backward trajectory analysis suggests transport from East Asia predominated in winter, whereas that from the Pacific Ocean predominated in summer. Spring and fall were transition seasons, with transport from both regions. The seasonal change of backward trajectory is consistent with the East Asia monsoon.
There were no obvious decline trends, but seems weak decline trends. Especially DDTs showed clear declining trends during the 8 year frequent sampling period. DDTs concentrations as well as the ratios of (o,p′ -DDT + p,p′ -DDT) to total DDTs, on the other hand, showed clear declining trends during sampling period, suggesting the decrease of input of newly produced DDTs in the regional environment by reflecting recent activities of Parties in the East Asian region to reduce/eliminate production and use of DDTs under the Stockholm Convention. DDTs isomers compositions shows that some data suggests different sources such as Dicofol impurities.
It shows similar seasonal trends and good correlation for Chlordanes, Heptachlors and Dieldrin especially high levels in 2010, 2011. It shows good correlation for HCBz and PeCBz due to the semi-volatile properties. New POPs shows detectable levels such as PeCBz, Endosulfans, HBCDs, PBDEs.
HCBD were highest levels in all POPs and all seasons. HCBD duplicate sampling data variations were within 30% with enough sensitivity. HCBD levels at super site were averaged 900pg/m^3 (330 – 2900 pg/m^3). HCBD concentration variation of 3 day continuous samples per month were 1.2 to 3.2 times differences. HCBD has correlation to HCBz, PeCBz, PCB, HCH, DDT. Data comparison of HCBD and $PM_{2.5}$ seems weak correlation. The Backward Trajectory analysis suggested that higher levels of $PM_{2.5}$ correlated to northwest wind direction affected from the Asian continent. HCBD levels are the highest POPs in ambient air due to the moderately high vapor pressure (20 Pa at 20℃) and is also released into air.

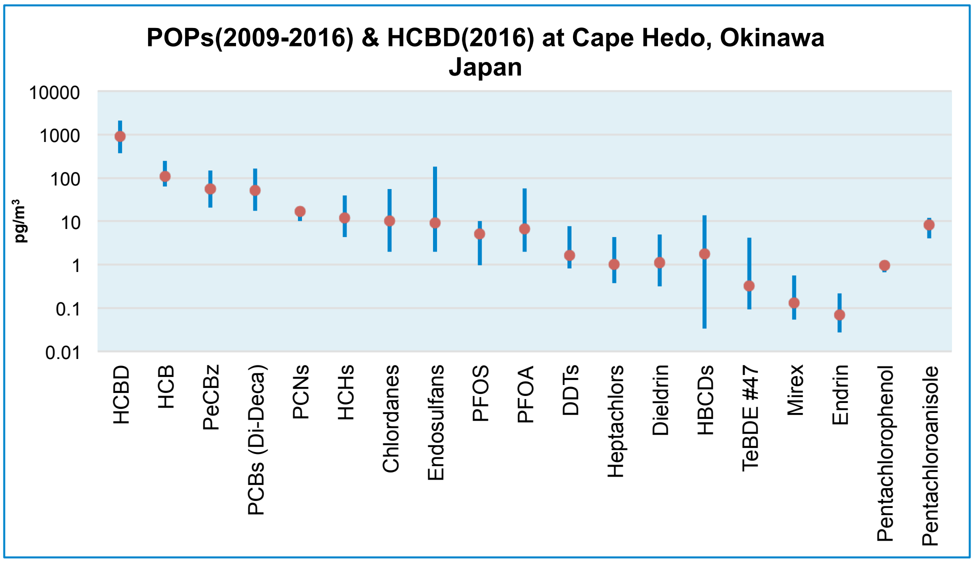

Fig1. POPs levels in FY 2009-2016

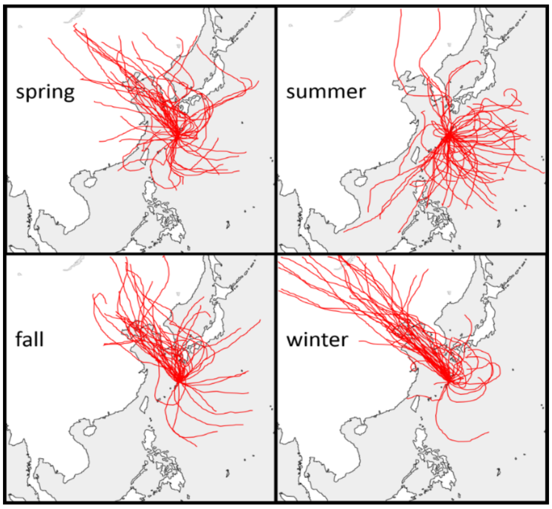

Fig2. The seasonal change of backward trajectory

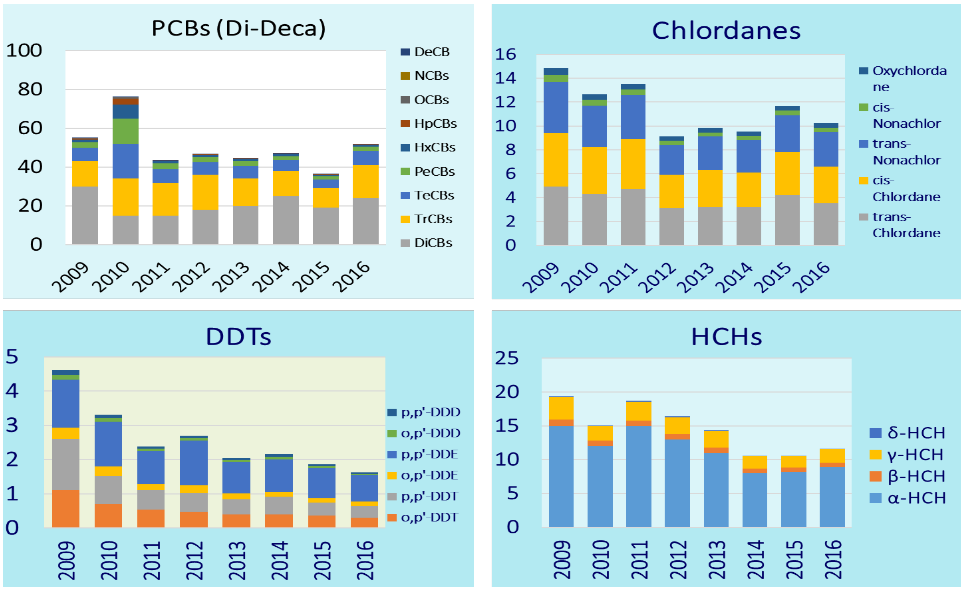

Fig3. POPs trends in FY 2009-2016

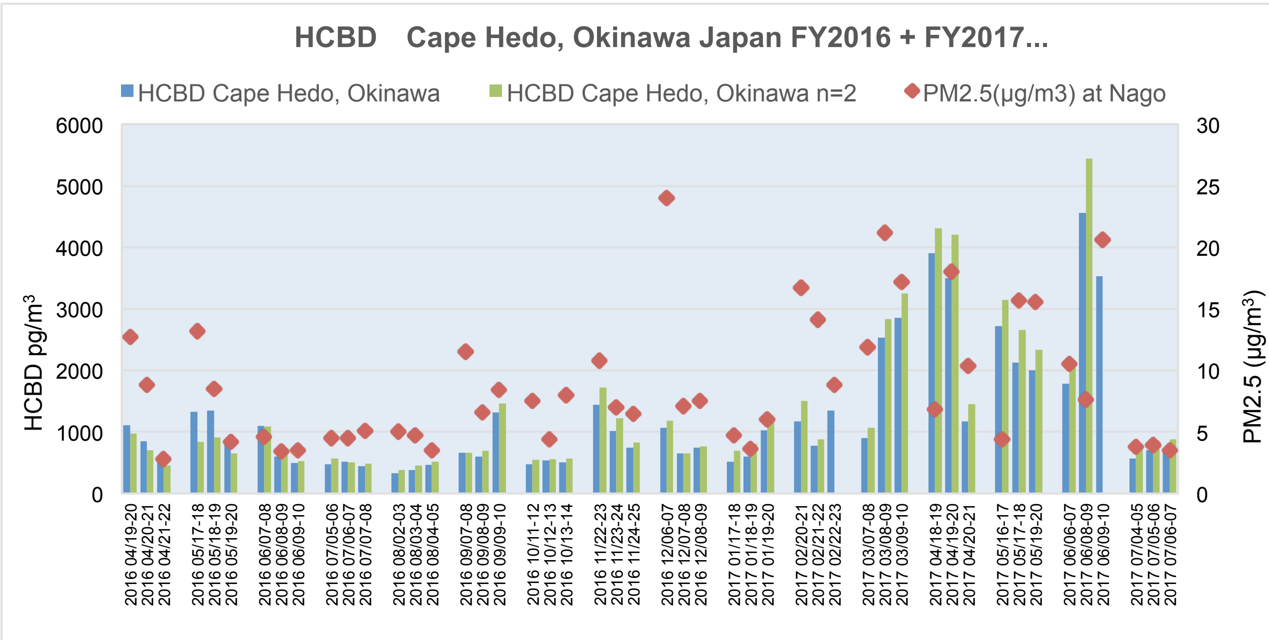

Fig4. HCBD trends in FY 2016 to 2017

References:

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3. Evaluation of new information in relation to the listing of hexachlorobutadiene in Annex C of the Stockholm Convention（UNEP/POPS/POPRC.12/INF/12/Rev.1, 2016）
4. T. Takasuga1, M. Yamashita, H. Takemori, T. Nakano, Y. Shibata, Dioxin2016 Florence POPs monitoring techniques and results from frequent monitoring of ambient air at super site, Japan

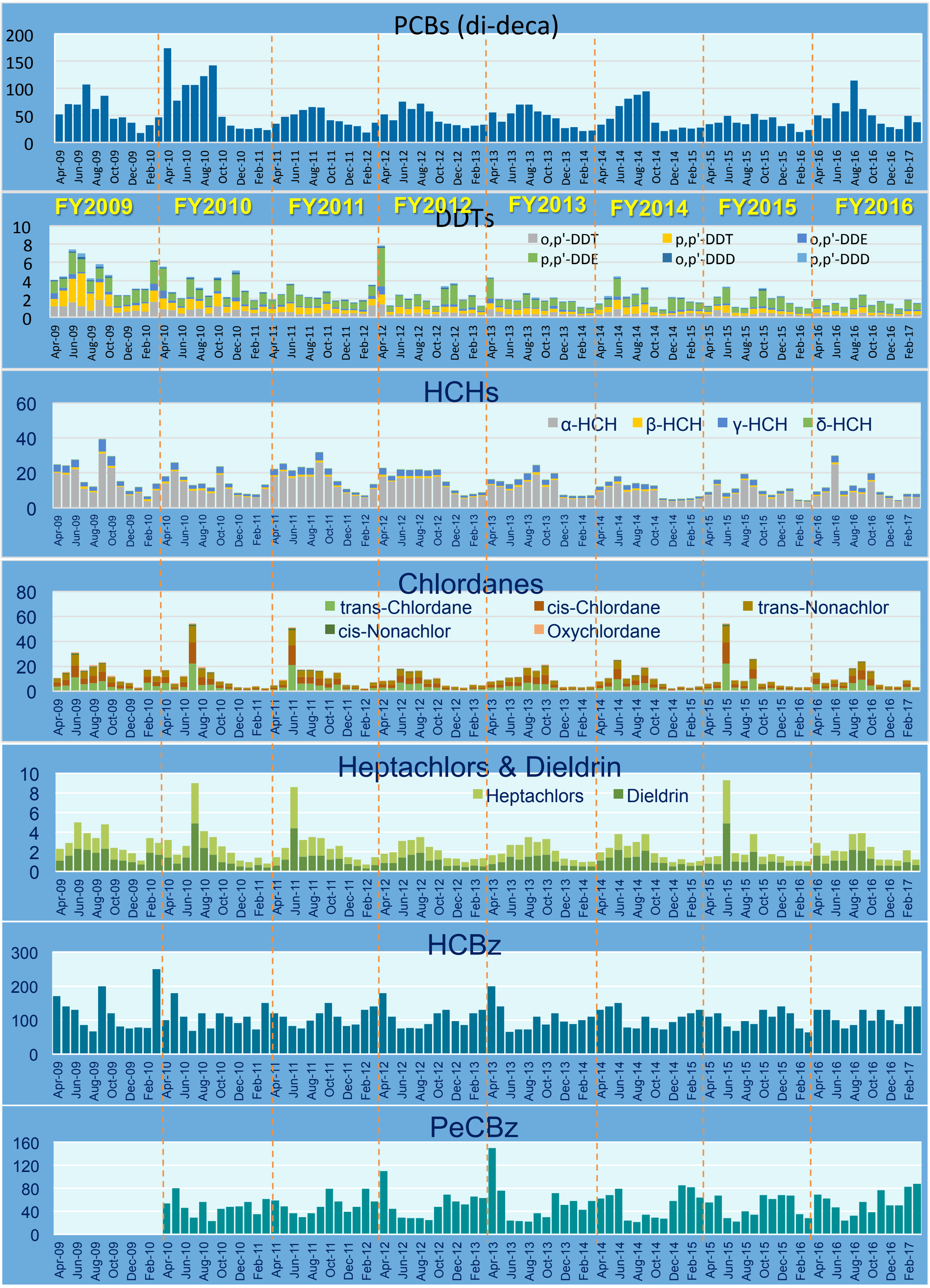

Fig5. Individual POPs trends in FY 2009-2016