POPS MONITORING TECHNIQUES IN AMBIENT AIR AND RESULTS FROM FREQUENT MONITORING AT SUPER SITE, JAPAN

Takasuga T[1]*, Nakano T[2], Shibata Y[3]

[1] Shimadzu Techno Research, 1, Nishinokyo Shimoai-cho, Nakagyo-ku, Kyoto 604-8436, Japan;
[2] Graduate School of Engineering, Osaka University, 2-4 Yamada-oka, Suita 565-0871,Osaka, Japan;
[3] National Institute for Environmental Studies, Onogawa16-2, Tsukuba, Ibaraki, 305-8506, Japan

Introduction

POPs are persistent in the environment and show a common property of long-range transport. Ambient air monitoring of POPs sampling and analytical methods should be designed carefully to assure the quality of the data as well enough sensitivity to cope with probable further decreases in environmental levels of POPs during long-term monitoring.
Following 21 chemicals (groups), out of 23 POP chemicals, with the exception of dioxins and furans, the analytical methods were established and evaluated as monitoring techniques from frequent monitoring in ambient air at southern supersite Japan. Data on their short-term spatial variations will contribute to a clarification and understanding of environmental transport and background levels in ambient air.

Materials and methods

- Monitoring station; Cape Hedo in Okinawa prefecture, Japan (N: 26.87, E: 128.26)
- Sampling; 3 days continuous sampling/month × 12month (36sample/y) since 2009. High volume (HV) air ampler 1,000 m^3 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 on the PUF before sampling.
- Additional trial: supplementary low volume (LV) air sampler 4m^3 2.8L/min, 24hrs for semi volatile POPs using PS Air cartridge.
- Method validation; evaluated under MOE POPs monitoring project

- High sensitive analysis by GC-HRMS (EI), GC-MS (NCI) and LC-MS/MS were evaluated.
- GC-HRMS analysis on DB-17HT GC column evaluated for 13grouping for 24 POPs with except with Endosulfan and Chlordecone.

Results and discussion

Technical Point for legacy & New POPs analysis are summarized as followings from method validation processes.

- Evaluated effective sampling using HV sampler with enough sampling efficiency for semi volatile POPs such as MoCB, DiCB, PeCBz, HCB, HCHs by supplemental LV sampler data.
- Extraction: separate extraction recomended for filter, PUF and ACF for target POPs.
- Comprehensive cleanup with legacy POPs and new POPs are summarized in Fig.1.
- Prevent photo degradation or thermal degradation should be taken for Brominated Flame Retardant(BFR).
- Specific method blank for PFOA etc. PFC (Teflon® material), for DecaBDE from laboratory materials and major legacy POPs from laboratory air which present background level should be consideration.
- Evaporation loss should be considered for semi volatile POPs such as PeCBz, HCB and HCH.
- Blank check for air sampler, adsorbent and laboratory equipment as well as laboratoriy air.

・ MDL, MQL, IDL, Methods Blank, Recovery, duplicate sampling were validated.

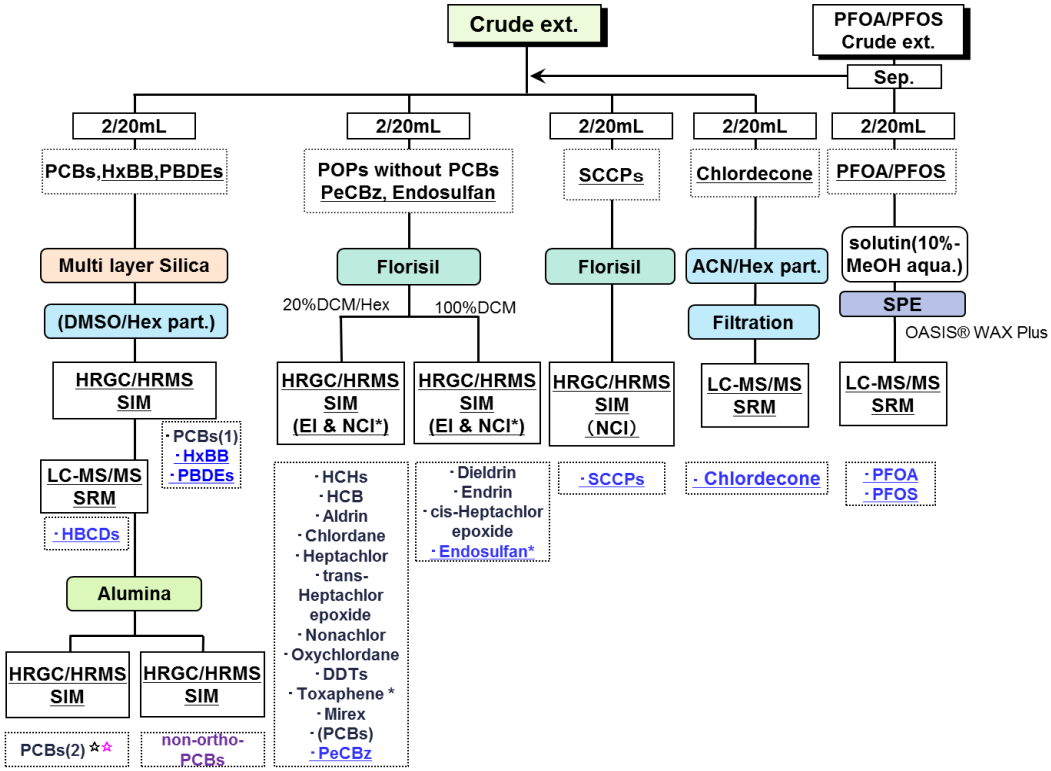

Fig.1 Comprehensive clean up flow chart for POPs in air sample

Results from frequent monitoring at supersite

It shows similar trends of POPs levels from FY2009 to FY2012 for frequent monitoring at super site in ambient air. The concentration orders were HCBz, PeCBz, and PCBs > HCHs > Endosulfans, Chlordanes, PFOS, PFOA, DDTs, and HBCDs > Heptachlors, Dieldrin, BDE (#47) and ND (not detected): HxBB, Chlordecone (Fig.2).

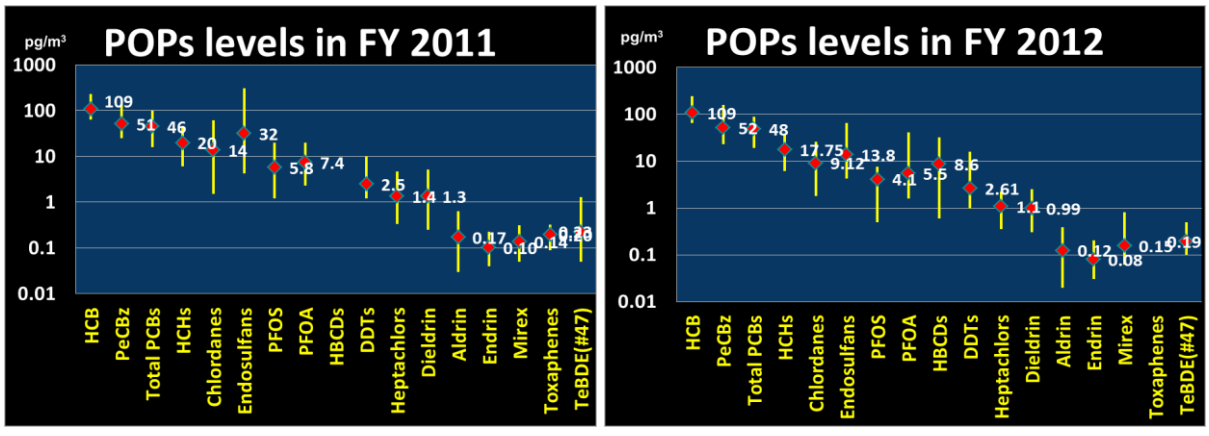

Fig.2 Concentration order of POPs in FY 2011 and 2012.

There were no obvious decline trends from 2009 to 2012 and generally higher level in warm season (Fig.3). It shows similar seasonal trends for Chlordanes, Heptachlors and Dieldrin in 2010, 2011. It shows good correlation for PCBs, HCBz and PeCBz from cluster analysis.

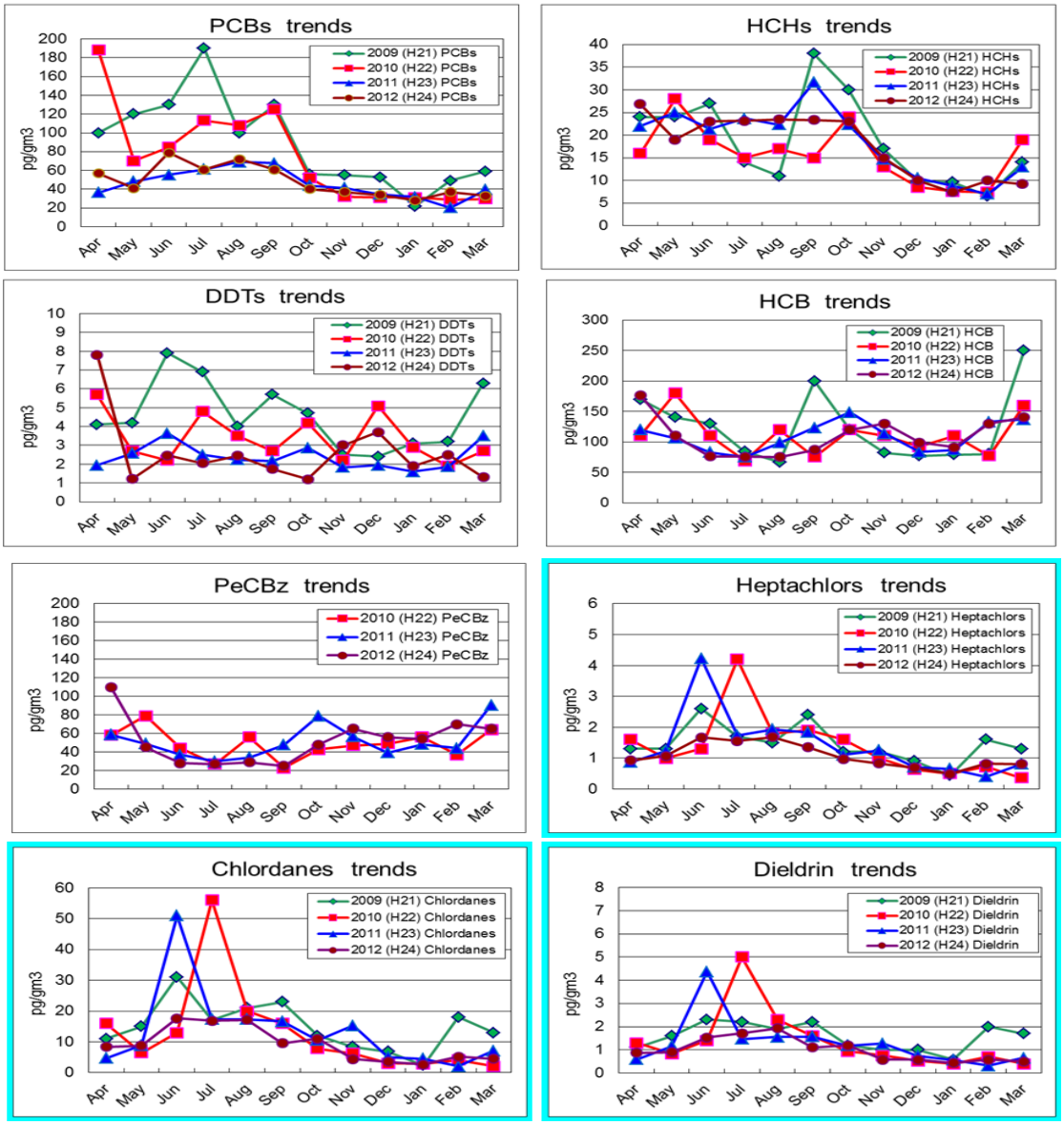

Fig.3 Seasonal trends for POPs in 2009-2012.

Backward trajectory trace shows seasonal wind direction. Generally winter season are northwest wind, spring season from mainland China, and summer season from Pacific Ocean or tropical region.

New POPs result shows detectable levels such as PeCBz, Endosulfans, HBCDs, PBDEs. Extremely tentative high levels of Endosulfans in Sep. 2011(data not shown) suggested domestic usage or atmospheric transport from mainland China.

Acknowledgements
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