

LONG RANGE TRANSPORT OF PERSISTENT ORGANIC POLLUTANTS AT HATERUMA ISLAND IN THE PERIOD FROM 2008 TO 2010

Takazawa Y*, Shibata Y

Center for Environmental Measurement and Analysis, National Institute for Environmental Studies (NIES), 16-2 Onogawa, Tsukuba, Ibaraki 305-8506, Japan

Introduction

Persistent organic pollutants (POPs) are, of the substances harmful to human health and the ecosystem, a group of organochlorine compounds that combine long range atmospheric mobility, bioaccumulativity and long-term persistence in an environment. The period that these POPs were generally used in Japan is assumed to be approximately 20 years from the 1950s, but upon actual analysis of river, ocean, air and living organisms, POPs continue to be detected from almost every sample, reflecting its persistency¹. This pattern is exactly equal on a global basis, but the major issue regarding POPs is that they are detected in considerably high concentrations even in high-latitude regions with no previous usage history, and that advective diffusion is progressing even today²⁻⁴. POPs readily vaporize in low-latitude regions, and are transported to higher latitude regions with the flow of the air. Once in high-latitude regions, they are assumed to descend and precipitate over the ground surface due to the cold climate, and consequently cause potential risk to human and high trophic level biota through the food chain. In other words, just as moisture generated indoors in wintertime becomes a condensation at the window, a form of irreversible mass transfer is established between the tropic low-latitude region and the frigid high-latitude region or the alpine region, and by repeating this process, POPs are transported a long distance⁵.

We have performed high-frequency observation of POPs using high volume samplers at Hateruma Island, which is located at the south end of Okinawa prefecture. Hateruma Island is located 2,000 km southwest of Tokyo, and was selected as a broad-based monitoring site representative of the East Asian region with little impact of regional pollution, in order to understand the long range atmospheric transportation (several thousand km) of POPs. The main purpose of this study is to clarify the current concentration of POPs in the East Asian region, specifically analyzing POPs contained in air samples collected at Hateruma.

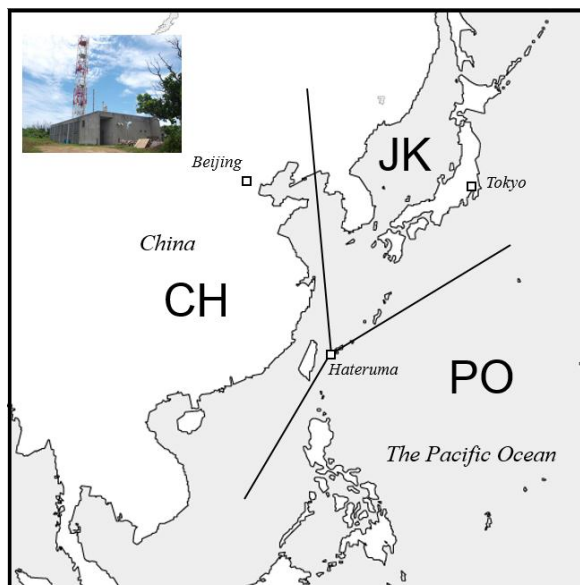


Figure 1. The location of Hateruma Island

Materials and methods

Hateruma Island is located at the southern end of the Japanese Archipelago, 60 km north of the Tropic of Cancer, 220 km east of Taiwan, and 460 km southwest of Okinawa. Hateruma island was formed by raised coral reef, and it is about 6 km east-west and 4 km north-south, with area of about 12.5 km². The population of the island is about 600 and the sugar cane farming is the island's main industry. The station is located at the east end of the island, about 100 m from the coast and 10m above sea level, surrounded by the windbreak forest. The wind is northerly to northeasterly in autumn-winter and southerly to southeasterly in spring-summer. The annual mean wind speed at the top of the tower (46.5 m above sea level) is about 8 m/s. The surface temperature is about 24°C and the annual rainfall is about 1900 mm. NIES ground-based station is located at the eastern end of the island (24° 3' 38" N, 123° 48' 33" E).

Twenty-one samples were obtained from November 2008 to September 2010 by use of a high-volume air sampler (SHIBATA Scientific Technology). The sampler was located on the top of the site building. Approximately 1,000 m³ of air mass was collected by operating the sampler under 700L/min (24 h in duration) once a month. Sampling sorbents consisted of a quartz fiber filter (200 mm width, 250 mm depth), polyurethane

form ($\phi 90$ mm, 100 mm height), and an activated carbon felt ($\phi 84$ mm, 2 mm height). The activated carbon felt was used as a backup filter of high volatile compounds such as HCB and HCH. The combination of sorbents was developed by NIES, and the POPs analysis method adopted by the Ministry of the Environment in Japan was based on NIES method including a cleanup procedure. Brief explanation of the cleanup procedure is described below.

Three sorbents were extracted with acetone and toluene, and the extracts were mixed. A crude extract was obtained by substituting the solvent of the mixture with hexane. Initially, dimethyl sulfoxide (DMSO)/hexane partitioning was applied to the crude extract. This partitioning was repeated, and the target compounds were transferred to 240 mL of hexane. The concentrate was purified on a pre-rinsed glass column containing the following packing materials (from top to bottom): 2 g of anhydrous sodium sulfate, 10 g of florisil, 2 g of anhydrous sodium sulfate, and a quartz wool plug. After sample loading, POPs were eluted with 100 mL of diethyl ether/hexane (5:95, v/v; fraction 1) and 100 mL of diethyl ether/hexane (20:80, v/v; fraction 2, dieldrin and endrin). Finally, Fraction 1 was evaporated to 5 mL before silica gel column chromatography. The pre-rinsed silica gel column contained the following packing materials (from top to bottom): 2 g of anhydrous sodium sulfate, 5 g of silica gel, 2 g of anhydrous sodium sulfate, and a quartz wool plug. After the concentrate of Fraction 1 was loaded, the organochlorine compounds were initially eluted with 30 mL of hexane (fraction 3, HCB, aldrin, and mirex) and then with 30 mL of diethyl ether/hexane (25:75, v/v; Fraction 4, containing the other POPs). Fractions 2, 3, and 4 were transferred to centrifuge tubes, and the solvent volume was reduced by a gentle stream of dry nitrogen. $^{13}\text{C}_{12}$ -labeled PCB153 (500 pg) was added as an internal standard to the final concentrate. POPs were determined using a high-resolution mass spectrometer JMS-700 (JEOL) equipped with a gas chromatograph 6890 (Agilent). The resolution of GC-HRMS was maintained at 10,000 throughout all the experiments.

Results and discussion

Four-day back trajectories were calculating using NOAA's ARL HYSPLIT model^{6,7}. The results are shown in Fig. 2. All trajectories calculated at 100 m were plotted. Transport from East Asia predominated in winter, whereas that from the Pacific Ocean predominated in summer. Spring and fall were transition seasons, in which transport from both East Asia and the Pacific Ocean was observed. The seasonal variation of back trajectory is consistently explained by a typical seasonal variation of the monsoon in this region. As shown in Fig. 1, the source region was divided into three classes (CH: china; JK: Japan-Korea; PO: the Pacific Ocean). The source region of each sample was determined by the position of intersection between the trajectory and the coastline. Trajectories without intersection were attributed to PO. In this study, twenty-one samples in all were obtained (CH: 6 samples; JK: 8 samples; PO: 7 samples). The mean total POPs concentration of each source region were as follows: 110 ± 28 pg/m^3 for CH, 180 ± 68 pg/m^3 for JK, and 105 ± 9.4 pg/m^3 for PO. Although the mean concentration of JK was higher than those of CH and PO, the mean concentration of PO was close to that of CH. The results of each sample were summarized in Figs. 3 and 4. POPs except HCB were detected with relatively low concentrations through the sampling period. The total concentration of POPs ranged from 66 to 300 pg/m^3 (average 130 pg/m^3). The highest POPs concentration and the ratio of HCB to the total POPs concentration were observed in February 2009. As seen in the four-day back trajectory result, the air mass collected in February 2009 originated from Korean coastal area. On the other hand, the total concentration of chlordane-related compounds (*cis*-/*trans*-chlordane, *cis*-/*trans*-nonachlor, and oxychlordane) varied from 0.9 to 9.0 pg/m^3 (mean 3.6 pg/m^3). Maximum concentration was obtained in November 2009, whereas minimum concentration was

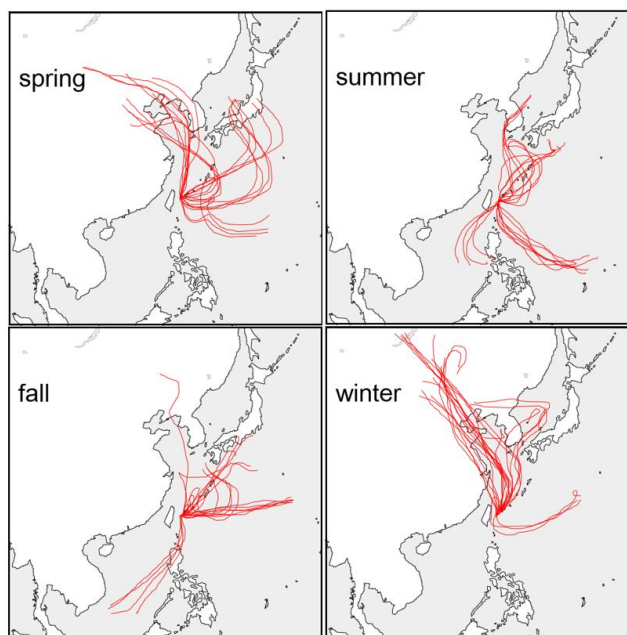


Figure 2. Four-day back trajectory analysis

showed in October 2009. As a result of the four-day back trajectory analysis for the sampling carried out in November 2009, it was clear that the air mass stayed around the main island of Okinawa. Chlordane insecticides have been widely sprinkled in Southeast Asia including Okinawa for termite control, the use of these products has been restricted since 1986 in Japan. It was thought that the use of chlordane products until recently provided the air mass with the impact. In contrast, the air mass for the sampling carried out in October 2009 originated from PO region.

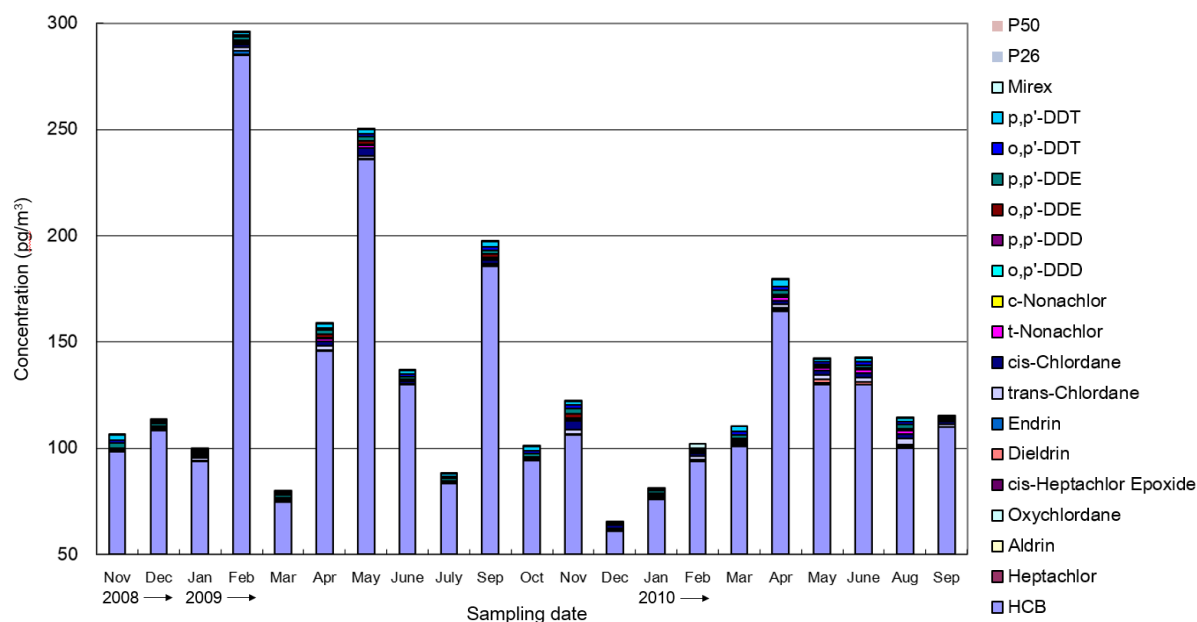


Figure 3. Concentrations of POPs observed at Hateruma Island

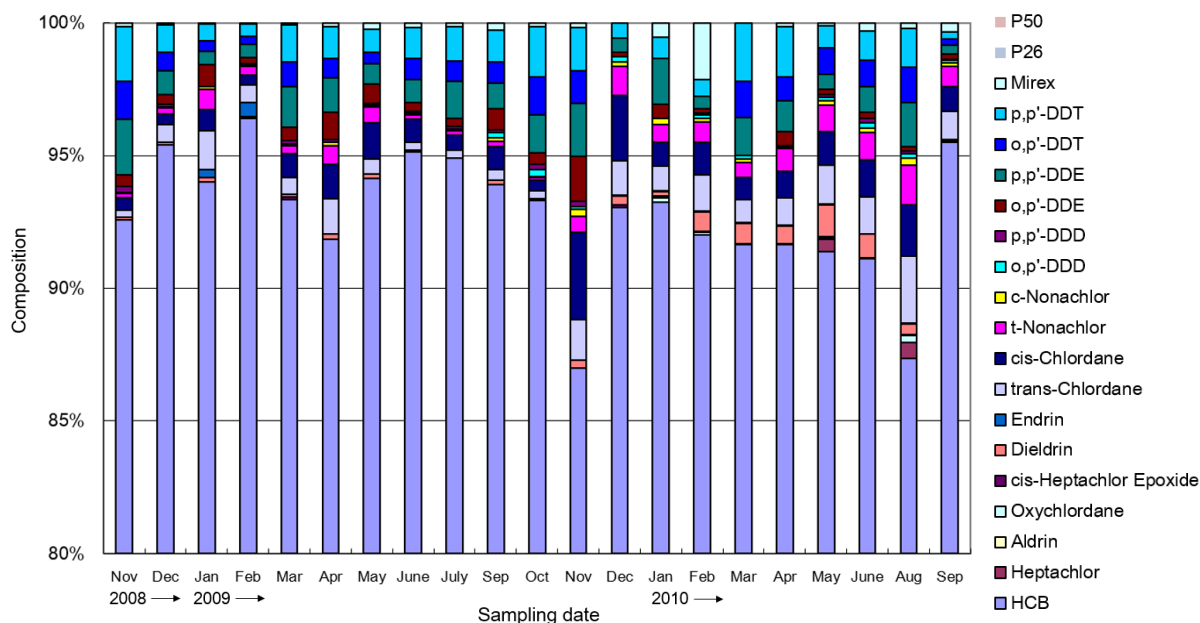


Figure 4. Compositions of POPs observed at Hateruma Island

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