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Recent decline of DDTs among several organochlorine pesticides in background air in East Asia☆

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ABSTRACT

Hexachlorocyclohexanes (HCHs), chlordanes (CHLs), and dichlorodiphenyltrichloroethanes (DDTs) in air-mass outflows from East Asia were recorded monthly from April 2009 to March 2014 at Cape Hedo in Japan. These organochlorine pesticides (OCPs) were collected by a high volume air sampler equipped with a quartz fiber filter, a polyurethane foam plug, and activated carbon fiber and analyzed by using a gas chromatograph–high resolution mass spectrometer. The overall (and geometric mean ± SD) concentration over the period was 4.9–43 pg m^{-3} (15 ± 7.8 pg m^{-3}) in HCHs (sum of α-/β-/γ-/δ-HCH), 1.5–83 pg m^{-3} (8.8 ± 11 pg m^{-3}) in CHLs (sum of *cis*-/*trans*-chlordane, *cis*-/*trans*-nonachlor, and oxychlordane), and 0.71–16 pg m^{-3} (2.5 ± 2.0 pg m^{-3}) in DDTs (sum of *o,p′*-/*p,p′*-DDD, *o,p′*-/*p,p′*-DDE, and *o,p′*-/*p,p′*-DDT). Clear seasonal changes, i.e. higher in summer and lower in winter, were observed in HCHs and CHLs, suggesting the dominant effect of temperature-dependence, secondary sources in these OCPs. DDT concentration as well as the ratio of (*o,p′*-DDT + *p,p′*-DDT) to total DDTs, on the other hand, showed clear a declining trend during the five year sampling period, suggesting the decrease of input of newly produced DDTs in the regional environment by reflecting recent activities in the East Asian region to eliminate production and use of DDTs under the Stockholm Convention.

1. Introduction

Our modern society is supported by variety of chemicals, and establishment and operation of sound chemical management system is a key to realize safe and sustainable development. Among tens of thousands of chemicals that have been developed and playing or once played essential roles in our daily life, some have toxicities as intentional (such as pesticides and pharmaceuticals) or unintentional (for example, PCBs, some of flame retardants, etc.) property and thus may pose potential risks to human health and wildlife depending on their properties as well as the amounts and the ways of their production, usage, or disposal. The Ministry of the Environment of Japan (MOEJ) has surveyed chemicals in the environment every year since 1974 to assess how much of various chemicals emitted to the environment during production, usage, and disposal remains in air, water, sediments, and wildlife (MOEJ, 1975). The survey, conducted at more than 150 sites nationwide, is instrumental in the early identification of environmental risks and in the planning and evaluation of control measures, and in the tracking of persistent organic pollutants (POPs).

As part of the activities to support Chemical Substances Control Law in Japan and the Stockholm Convention, the MOEJ monitors POPs in water, sediments, air, and living organisms. POPs are toxic, highly bioaccumulative, and persistent in environment, with long-range transport potential through air, water or by immigrating organisms (Jones and de Voogt, 1999; Stockholm Convention, 2001). Many intentional POPs had been used in Japan for a couple of decades and were banned in 1970's/early 1980's. Their environmental concentration in Japan showed clear declining trends through 1970's/1980's, but they continue to be detected in environmental samples, reflecting their persistence (JPPA, 1970; Tanabe et al., 1994; Murayama et al., 2003; Hogarh et al., 2013; MOEJ, 2015). In addition to the nationwide yearly monitoring, MOEJ also took initiative to start POPs monitoring in air at background sites in East Asia in order to support effectiveness evaluation under the Article 16 of the Stockholm Convention. Following to the first workshop held in Tokyo on November 2002, the first phase of the background air POPs monitoring in East Asia was conducted through

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2004–2007. The results were compiled as the first sub-regional report, and submitted through focal point of each country to the Stockholm Convention to be included in the 1st Regional report in Asia-Pacific (Stockholm Convention, 2008). The program continues and the data from 2008 was included in the 2nd Regional report in Asia-Pacific (Stockholm Convention, 2015).

As part of background air POPs monitoring in East Asia program, Japan has been conducting air monitoring in remote islands in south-western part of Japan. Initially the monthly monitoring was conducted in Hateruma Island during April 2004–September 2010 by the National Institute for Environmental Studies (NIES) in order to establish high frequency monitoring site in East Asia as well as to develop inexpensive and automated monitoring method. Since April 2009, POPs in air have been monitored at Cape Hedo in Okinawa Island by MOEJ with the same analytical method as that used for nationwide monitoring. Among various POPs chemicals, we selected hexachlorocyclohexanes (HCHs), chlordanes (CHLs), and dichlorodiphenyltrichloroethanes (DDTs) in this study. HCHs showed considerably greater historical usage than other organochlorine pesticides (OCPs) in East Asia (Li and Macdonald, 2005). China produced technical HCHs until 1983, manufacturing about 4.9 million t, or 33% of total world production (Fu et al., 2003). Japanese production of HCHs reached 315,000 t as technical HCHs and 9532 t as lindane during 1958–1970 (JPPA, 1970). Besides being used as pesticide, CHL has been used as termiticide particularly in tropical region. During 1980's, Japan imported 1000 to 2000 t year^{-1} of CHLs, part of which was directly applied around homes and used as a termiticide during the manufacture of veneer board (Nishimoto, 1983). China also used CHLs until its ban in 1999 (Wong et al., 2005). DDT is also one of most produced OCPs in the world. The cumulative world production of DDT has been estimated as 2 million t (ATSDR, 2002). Although its use as pesticide were banned in many Asian countries including Japan well before the ratification of the Stockholm Convention, it was listed in Annex B of the Convention, which allowed its production and use for specific purposes. i.e., vector control in tropical region and material for the synthesis of another OCP, dicofol. In addition to their usage amounts, the differences in their production histories as well as their chemical properties make them attractive target combinations in East Asian environment.

This paper reports the concentration of HCHs, CHLs, and DDTs based on monthly air observation at Cape Hedo from April 2009 to March 2014.

2. Materials and methods

2.1. Sample collection

Cape Hedo is located at the far northern end of Okinawa Island (Fig. 1). Northern part of the island is a heavily forested area, called "Yambaru", which occupies 30% of the land area of the island with only 0.8% of the population. As there is no substantial human activity in the nearby area, Cape Hedo is appropriate for background air observation, and a national acid deposition observation site (MOEJ) and Cape Hedo Atmosphere and Aerosol Monitoring Station (NIES) were set side by side. A total of 336 samples were collected at MOEJ site in three consecutive days every month in duplicates (except in FY 2013 where duplicate sampling was done in one among the three consecutive days) between April 2009 and March 2014. A high-volume air sampler (SIBATA Scientific Technology, Inc.) passes 1000 m^3 of air per 24 h at 700 L min^{-1} through three adsorbents in the order of: a quartz fiber filter (QFF), a polyurethane foam plug (PUF), and activated carbon fiber (ACF). The QFF collects the particulate matter. The PUF (spiked with ^{13}C-labeled OCP surrogates, 2000 pg each) collects the majority of the semivolatile

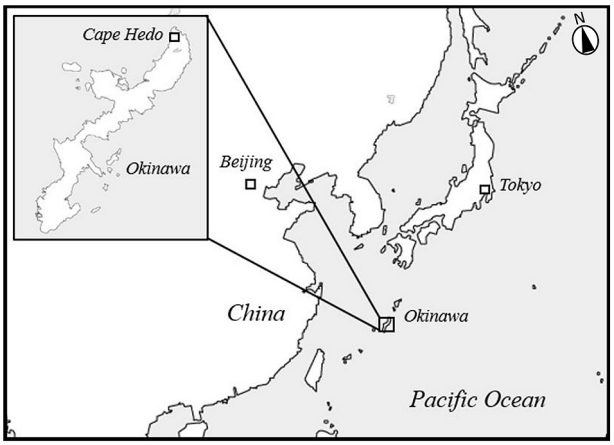

Fig. 1. Regional map showing the location of Cape Hedo.

compounds in gas phase, while some with higher volatility, such as α-HCH, can easily break through the PUF and are trapped by a stronger adsorbent, ACF. Air was sampled in three 24-h runs over three consecutive days. After sampling, the adsorbents were sealed stored at 5 °C until analysis. All procedures including chemical analysis were conducted by Shimadzu Techno-Research (Kyoto, Japan).

3. Materials

Acetone, hexane, toluene, and dichloromethane were purchased from Kanto Chemical (Tokyo, Japan). Decane and Florisil were the products of Wako Pure Chemical Industries (Osaka, Japan). The blank levels of organic solvents were sufficiently low. Authentic standards (α-/β-/γ-/δ-HCH, *cis*-/*trans*-chlordane, *cis*-/*trans*-nonachlor, oxychlordane, *o,p′*-/*p,p′*-DDD, *o,p′*-/*p,p′*-DDE, *o,p′*-/*p,p′*-DDT, $^{13}C_6$-α-/β-/γ-/δ-HCH, $^{13}C_{10}$-*trans*-chlordane, $^{13}C_{10}$-*cis*-/*trans*-nonachlor, $^{13}C_{10}$-oxychlordane, $^{13}C_{12}$-*o,p′*-/*p,p′*-DDD, $^{13}C_{12}$-*o,p′*-/*p,p′*-DDE, and $^{13}C_{12}$-*o,p′*-/*p,p′*-DDT) were purchased from Cambridge Isotope Laboratories (Andover, USA). An internal standard ($^{13}C_{12}$-PCB70) was purchased from Wellington Laboratories (Guelph, Canada). The QFF and PUF were the products of SIBATA Scientific Technology (Soka, Japan) and the ACF (KF-1500) was made by Toyobo (Osaka, Japan) and were used after the pre-cleaning with acetone and toluene in a Soxhlet extractor in the same manners as the cleanup procedure.

4. Chemical analysis

4.1. Extraction and cleanup

The QFF and ACF were extracted with acetone for 2 h and toluene for 16 h in a Soxhlet extractor. The PUF was extracted only with acetone for 16 h. The crude extracts were concentrated and mixed and then dried by evaporation. Florisil columns were packed (from top to bottom) with anhydrous sodium sulfate, 8 g of Florisil adsorbent, anhydrous sodium sulfate, and a quartz wool plug. After the rinse with dichloromethane/hexane (20:80, v/v), each sample was loaded. OCPs were eluted with 80 mL of dichloromethane/hexane (20:80, v/v). The eluate was concentrated and transferred to glass tubes, and $^{13}C_{12}$-PCB70 (250 pg) was added to each tube as an internal standard. The solvent volume of the eluate was reduced by a gentle stream of dry nitrogen, and the final concentrate was transferred to micro glass tube dissolved in decane.

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