MIREX AND TOXAPHENE IN ATMOSPHERE AND PINE NEEDLE COLLECTED IN JAPAN

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Introduction

Over the past three decades, remarkable vast economic growth has occurred in East and Southeast Asian countries. They have been industrialized and have produced many kinds of chemicals for their economic activities. Consequently, these compounds have been released to the environment and have been transported to the other countries. Persistent organic pollutants (POPs), which are one of man-made organic chemicals, are persistent and bioaccumulative. They tend to be dispersed by long-range atmospheric transport. They are likely to cause significant adverse effects to wildlife and humans. Under the 2001 Stockholm Convention[1], POPs monitoring program was started by the Japanese Ministry of Environment in 2002 in order to understand the status of POPs contamination in the environment of Japan. A notable finding was that mirex and toxaphene were detected in wildlife and air samples [2]. This may be due to cross border contamination, because the both chemicals had never been registered in Japan [2]. However, existing analytical data of the compounds in the environment of Japan are still limited so far [3-5].

In the present study, residue levels of mirex and toxaphene in the atmosphere and pine needle samples collected from the Japanese territory, including southern parts of sea areas around Japan and its adjacent areas, were measured to determine the cross border contamination of the chemicals from the East Asian countries to the Japanese territory.

Materials and methods

Marine atmospheric samples were collected from the Nansei Islands (Ryukyu Islands), northern East China Sea and southern Japan during the period from June in 2009 to July in 2010. Some atmospheric and pine needle samples were collected from Shikoku and Honshu Islands of Japan in the periods. The target compounds in the atmosphere were sampled by quartz fiber filters, polyurethane foam resin and activated carbon filters which were assembled in a cartridge. An average volume of each air samples was 1000 cubic meters. The quartz fiber filters and adsorbents for air samples and pine needle ones were respectively extracted with acetone and toluene in Soxhlet apparatus. Then, interfering substances were eliminated by sulfuric acid treatments. Subsequently, we performed further clean-up by column chromatography, with Florisil and silica-gel as adsorbents, and liquid partitioning with dimethyl sulfoxide/hexane.

Toxaphene is a complex mixture and a limited number of its constituents (Parlar #26, Parlar #40 + #41, Parlar #44, Parlar #50 and Parlar #62) were analyzed as target compounds. ^{13}C-mirex (Cambridge Isotope Laboratories, Inc., USA), ^{13}C-*trans*-chlordane (Cambridge Isotope Laboratories, Inc., USA), ^{13}C-hexachlorobiphenyl (#138) (Wellington Laboratories, Inc., USA) and ^{13}C-pentachlorobiphenyl (#111) (Wellington Laboratories, Inc., USA) were used as internal standards for clean-up spike for mirex and toxaphene, and syringe spike, respectively. Prior to this analysis, we carried out recovery tests, spiking ^{13}C-labeled mirex and ^{13}C-labeled *trans*-chlordane into air and pine needle samples. The average recovery for those compounds was more than 70 %.

A high resolution gas chromatograph (HRGC) (GC: Agilent Technologies, Model HP-6890, USA) and a high resolution mass spectrometer (HRMS)(MS: JEOL Limited, Model JMS-800D, Japan) were used in the analysis of mirex and toxaphene. The GC columns employed were: HT-8(60 m length, 0.25 mm I.D., Kanto Chemical Co., Inc., Japan) for mirex; DB-5MS (30 m length, 0.25 I.D., 0.25μm film thickness, J & W Scientific Inc., USA) for toxaphene. GC conditions for HT-8 and DB-5 were as follows: from 120 °C to 180 °C at a rate of 20 °C/min, then increased to 290 °C at a rate of 4 °C/min, held for 9.5 min. The MS conditions for both compounds were as follows: 260 °C for ionization temperature; 38 eV for ionization voltage; 500 μA for ionization current; 10 kV for accelerating voltage. Resolution of the mass spectrometer was greater than 10,000 with electron ionization spectrometry in the selected ion monitoring mode (GC/HRMS-SIM). Two selected fragment ions were monitored for each compound.

The following quantifiable conditions were applied to all analytical data, 1) the retention time of the native was within 0.5 seconds of the corresponding ^{13}C-labeled compounds, 2) the isomer ratio of the two monitored masses was within 15% of the theoretical value, 3) the signal/noise ratio was more than 3 for quantification, 4) for every series of analytical runs, ^{13}C-labeled standards were added to the samples, and the recovery of the added ^{13}C labeled internal standards was more than 70 %, 5) for each series of samples, the blank values of the complete quantification procedures were determined, and sufficiently low blank values were obtained. The limit of detection (LOD) was estimated at 3 standard deviations of the blank (obtained from three analyses).

Results

Atmospheric Sample

Mirex was detected in various levels. The concentrations ranged from less than LOD to 0.227 pg/ m^3. Mirex concentrations were different in the areas and the seasons. The highest concentration (0.227 pg/m^3) was found in the sample collected from the nothern East China Sea in summer and a relatively low concentration (0.008 pg/m^3) was found in the samples collected in the Honshuu Islands in winter. The relatively low concentratins were detected in the samples collected in the cold season. On the other hand, the toxaphene concentrations were less than the values of detectable limit. In detail, the values of #26, 40/41, 44, 50 and 62 were 0.17, 0.03, 0.05, 0.16 and 0.08 pg/m^3, respectively.

Pine needle Sample

Mirex was detected in the almost all of the samples analysed. The concentration was ranged from 1.04 to 9.35 pg/g on wet weight basis in the samples collected in Japan. A narrower concentration range of mirex was observed in the pine needle samples than those in the atmospheric samples. On the other hand, some pine needle samples collected in neighboring countries were analysed tentatively, and as a result, a relatively high concentrations of mirex were determined in the samples of neighboring countries. As the same manner for the atmospheric samples, toxaphene was not detected in any pine needle samples.

Discussion

Although the analytical data of mirex in the Chinese air samples are limited so far, Lammel et al. reported that mirex was found in the all samples, ranging from 6.7 to 255 pg/m^3 , and 79 pg/m^3 on average, in the air of coastal urban area, Qingdao, China (36^{0}05'N, 120^0 20'E) [6]. The concentrations were hundred times or thousand times higher than the figures obtained in the present study.

To clarify the correlation between the mirex concentrations and a current of air for the different sampling sites and periods, back trajectory analysis supported by National Institute of Environmental Studies, Japan, was performed to investigate a current of air during different seasons. The results of all of the trajectories indicated that the flow of air arrived on February was originated in Russia. On the other hand, it was also clear that the flow of air arrived in June and July originated in the southern China and Southeast Asian countries. The study showed that the northern air was clean (low concentation of mirex). In contrast, the air masses that arrived in

June and July carried more anthropogenic pollutants. The air parcels passed through the southern China, where much amounts of mirex might be used for such as termite control or the other industrial purposes.

Mirex was applied for insect control or a fire retardant in plastics, rubber, paint, paper, and electric goods during from early 1960s to mid-1970s in U.S. and Canada [7, 8]. Its use has been banned since 1976 because of its undesirable environmental effects [7, 8]. Though it was a little too late, China started researches and developments of mirex in 1969 [9]. It has been estimated that the amount of the cumulative production of mirex was 151 tons in China [10]. In July 2006, the "Demonstration project of Alternatives to Chlordane and Mirex in Termte Control in China" was initiated to eliminate the production and use of mirex [9]. However, China did not completely eliminate the production and use of mirex until May in 2009 [11]. It has mainly used for termite control in residential and other buildings [9]. Mirex was never registered in the Chinese Ministry of Agriculture, and was not used as pesticide for agriculture [12]. Recently, contamination of POPs has been reported in Chinese samples such as water or sediment of the River Yangtze [13, 14, 15]. There are many chemical industrial complexes along the river and at the lower coastal area [16, 17]. Particularly, all the mirex manufactures are located in Jiangsu Province, which is located in the downstream area of the River Yangtze [11]. In conclusion, some results of the present study demonstrated that southern China might be one of the mirex pollution sources toward Japan.

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