MIREX AND TOXAPHENE IN SURFACE SEAWATER COLLECTED FROM THE NANSEI ISLANDS AND NORTHERN EAST CHINA SEA

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Introduction

Recently, East and Southeast Asian countries have industrialized and have produced many kinds of chemicals for their economic activities. Consequently, these compounds have released to the environment and have transported to the other countries. Persistent organic pollutants (POPs) which are one of man-made organic chemicals, are persistent and bioaccumulative, tend to long-range atmospheric transport and deposition, and are likely to produce 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 Japanese environment. A notable finding was that mirex and toxaphene were determined 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 Japanese environment are still limited so far [3, 4].

In the present study, residue levels of mirex and toxaphene in surface seawater collected from the southern parts of sea areas around Japan were determined to evaluate the contamination status of the chemicals in the Japanese marine environment.

Materials and methods

The surface seawater samples (n=13) were collected from the Nansei Islands (Ryukyu Islands) and northern East China Sea, southern Japan during the periods of June to July, 2009. The target compounds in seawater sampled by adsorption with column containing XAD-2 resin, polyurethane foam and activated carbon filter. An average volume of each seawater sample was 500 L. The adsorbents for seawater samples were extracted with acetone in Soxhlet apparatus. Then after, interfering substances were eliminated by sulfuric acid treatment. Subsequently, we performed further clean-up using column chromatography with Florisil and silica-gel as adsorbents. Toxaphene is a complex mixture, and so 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 analysis, we carried out recovery tests, spiking ^{13}C-labeled mirex and ^{13}C-labeled *trans*-chlordane into seawater 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/EI-HRGC-SIM). Two selected fragment ions monitored for each compound.

The following quantification conditions were apply for 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 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 and Discussion

The concentrations of toxaphene were less than the values of detection limit. On the other hand, mirex was detected with high detection frequency in the samples collected from the Nansei Islands and the northern East China Sea. The concentrations ranged from less than limit of detection to 0.083 pg/L. The highest concentration found in the sample collected from off Okinawa Island in the Nansei Islands. However, mirex concentrations determined in the seawater samples collected from the northern East China Sea were higher than the concentrations in the samples collected from the Nansei Islands with the exception of one sample. In detail, the concentrations ranged from 0.010 to 0.039 pg/L in the samples collected from the northern East China Sea. Furthermore, among the concentrations measured in the samples collected from the northern East China Sea, the concentrations obtained from western north sites were higher than the figures from other sites of the northern East China Sea. A statistically significant difference was observed between the mirex concentrations obtained from the both sea areas as the results of Mann-Whitney U-test.

Mirex was applied to fields for insect control and a fire retardant in plastics, rubber, paint, paper, and electric goods during early 1960s to mid-1970s in U.S. and Canada [5, 6]. The use has been limited since 1976 because of its undesirable environmental effects [5, 6]. Though a little too late, China started research and development of mirex in 1969 [7]. It has been estimated that the cumulative production of technical grade mirex was 151 tons in China [8]. In July 2006, the “Demonstration project of Alternatives to Chlordane and Mirex in Termte Control in China” was initiated to eliminate the production and usage of mirex [7]. However, China did not completely eliminate the production and use of mirex until May, 2009 [9]. It has mainly used in termite control in residential and other buildings [7]. Mirex never registered in the Chinese Ministry of Agriculture, and does not used as a pesticide for agriculture [10]. Recently, contamination of POPs has been reported in Chinese environmental samples such as water and sediment samples from the River Yangtze [11, 12, 13]. There are many chemical industrial complexes along the river and at the lower reach [14, 15]. Particularly, all the mirex manufactures are located in Jiangsu Province, which lies in the downstream area of the River Yangtze [9]. The vast volume of fresh water of the river flows into the East China Sea. The fact calls us to mind that the river may be one of contamination sources of the anthropogenic chemicals to the East China Sea. Consequently, the relationships between the mirex concentrations and salinities were investigated on each sample analyzed in the present study. However, any relationships did not observe. Although the data of mirex in seawater of China are limited, recently, Jia et al. reported mirex concentrations in seawater samples collected from the Bohai and Yellow Seas in shore around Dailian, northeast China [16]. It is a fact worthy of attention that the concentrations of mirex in the seawater collected from the shore around Dailian [16] are about three orders of magnitude larger than the concentrations determined in the present study in the seawater samples collected from the northern East China Sea. It suggests that China could be one of sources for mirex contamination in East China Sea.

It is important to mention that this survey covers only the waters of limited areas and an extensive survey in the Chinese side of East China and Yellow Seas covering may reveal a different contamination status altogether. Furthermore, it is necessary to assess potential contributions to mirex contamination in seawater from the other Asian countries.

Although it is difficult to identify the contamination sources, it is safe to say that mirex contamination determined in the present study in the territorial waters of Japan may be cross border contamination from foreign countries.

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