HRGC/HRMS ANALYSIS OF MIREX IN SOIL IN LIYANG, CHINA

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Abstract

China is a country with the greatest diversity of termites and the most severe termite damage in the world. Mirex has been widely used in China for termite control. Liyang city, located in the south of Jiangsu Province, China, is an important production base of mirex. Soil samples were collected from 23 sites in Liyang city in February, 2009. HRGC/HRMS (high-resolution gas chromatography /high-resolution mass spectrometry) was employed for mirex analysis. It was found that the detected levels of mirex in soil in Liyang were 2.9 ~ 4300 pg/g dw (dry weight), with the geometric mean 26.83 pg/g dw and the geometric standard deviation 5.02. The highest level occurred at the site near the Guanghua Chemical Company, which has produced mirex for more than 10 years. It implied the contribution of industrial activities to the mirex levels in the environment in Liyang city. However, the emission from the factory only influenced a rather limited adjacent area. The distribution and fate of mirex in Jiangsu Province were also discussed using fugacity model. It is estimated that the total amount of mirex in the environment in Jiangsu province is about 460 kg. Most of the mirex existed in soil, accounting for more than 95% of the total amount of mirex.

Introduction

China is a country with the greatest diversity of termites and the most severe termite damage in the world. Mirex, widely used in China for termite control, is highly persistent and its residue has been detected in water, soil, sediment, breast milk and human tissues for as long as 12 years after exposure [1]. In China, all the mirex manufacturers were located in Jiangsu Province. In Jiangsu Province, there has been a very important mirex enterprise, Liyang Guanghua Chemical Company, which is located in Liyang. Although Liyang is an important production base of mirex, the pollution status of mirex has not been determined and reported. It is necessary to determine and evaluate the pollution level and the environmental behaviors of mirex in Liyang. In this study, 23 soil samples were taken from Liyang to determine the pollution status of mirex using HRGC/HRMS (high-resolution gas chromatography /high-resolution mass spectrometry) method. The distribution and fate of mirex in Jiangsu Province were also discussed using fugacity model.

Materials and Methods

Sampling

The sampling campaign was conducted in the Liyang city, China in February, 2009. The sampling sites are

shown in Fig. 1. DIK-115B soil sampler was used for soil sampling. Sixteen soil samples (No. 1~16) were respectively taken from the 16 grid units (Fig. 1). Around the mirex enterprise, Liyang Guanghua Chemical Company, seven more samples (No. 17~23) were taken. In total, 23 soil samples were taken.

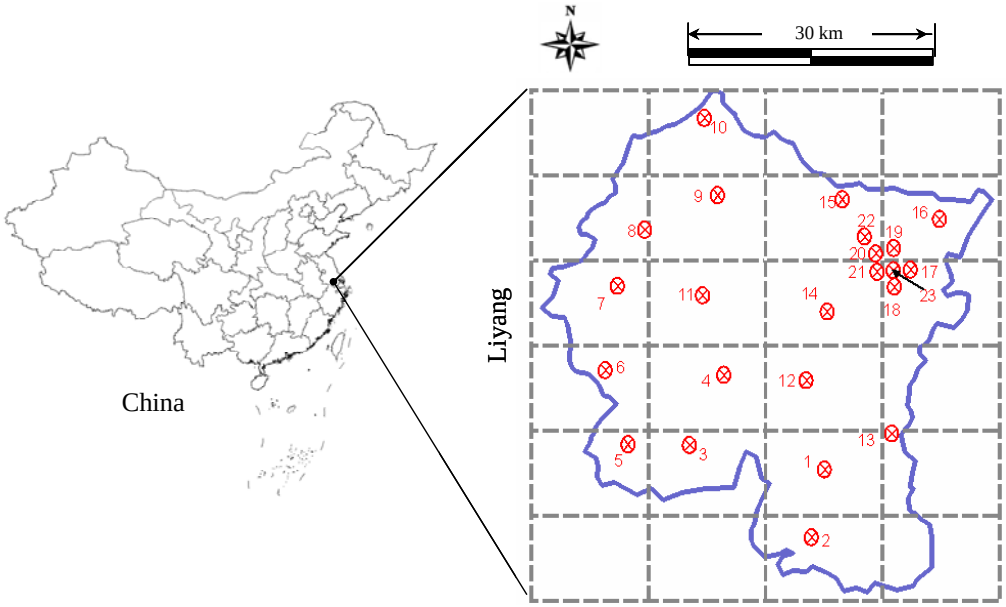

Fig. 1 Sampling sites in Liyang, China (Site 23 located at 50m away from the Liyang Guanghua Chemical Company.

Sample preparation and HRGC/HRMS analysis

The sample preparaiton and HRGC/HRMS analysis procedure for mirex analysis of soil samples are shown in Fig.2.

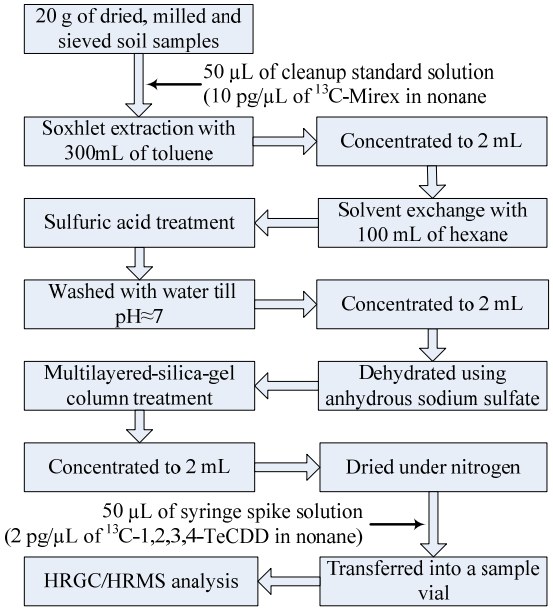

Fig. 2 Sample preparation and HRGC/HRMS analysis Procedure for mirex analysis in soil

Multimedia fugacity model Simulation of mirex in Jiangsu province

A level III multimedia fugacity model was developed and applied to simulate the distribution and fate of *mirex* in Jiangsu Province of China based on an approach of Mackay [2,3]. Four bulk compartments including air (air and particulates), water (water, suspended solids, and fish), soil (air, water, and solids), and sediment (water and solids) were included in the model.

Results and discussion

Comparison of mirex levels

To our knowledge, in the published papers and reports, the HRGC/HRMS method has never been used for mirex

analysis in soil samples in China. In most cases, the detection ratio of mirex in environmental media is rather low using conventional GC/MS methods due to its low concentration [4,5]. For GC/MS method, usually, the LOD (Limit of Detection) is about 0.01 ng/g dw; LOQ (Limit of Quantification) is about 0.1 ng/g dw. In this study, HRGC/HRMS was employed in mirex analysis, and mirex was detectable in all the soil samples. For the HRGC/HRMS method in this research, the LOD is 0.125 pg/g dw, the LOQ is 0.5 pg/g. The HRGC/HRMS method is much more sensitive than GC/MS method. In China, the consumption of mirex was not very large [1,6,7], therefore, in most cases, the mirex levels in environment were so low that GC/MS might be not applicable to mirex analysis in China. HRGC/HRMS is preferable in mirex analysis in the environment media.

The detected levels of mirex in the soil samples taken from Liyang were 2.9 ~ 4300 pg/g dw, which were much lower than the primary remediation target for mirex in soil for 9 districts of USA (270 ng/g for residential areas, 960 ng/g for industrial areas). The highest level, 4300 pg/g dw, occurred at the sites near the Guanghua Chemical Company, which has produced mirex for more than 10 years. It implied the potential contribution of industrial activities to the mirex levels in the environment in Liyang city. At site 20, which is located at the 2 km leeward from the Guanghua Chemical Company, the second highest mirex level, 220 pg/g dw, was observed. Mirex level sharply decreased to 50 pg/g dw at the site 22, which is 4 km leeward from the factory. For the four sites 2 km away from the factory in different directions (2 km east, south, west and north from the Guanghua Chemical Company), the concentrations were 22~140 pg/g dw, with the geometric mean 58.49 pg/g dw, which were much higher than the mirex levels in the 16 soil samples from the 16 grids (No.1~16).

Statistical distribution of mirex in soil in Liyang

A Kolmogorov-Smirnov (KS) test was performed to determine whether the normal or lognormal model was applicable for fitting the spatial distribution of mirex (SPSS v13.0). The concentrations of mirex in soil in Liyang city generally obey lognormal distribution (Kolmogorov-Smirnov Z = 0.618, Asymp. Sig. (2-tailed) = 0.840) (Fig. 3). The geometric mean is 26.83 pg/g dw and the geometric standard deviation is 5.02. From Fig. 3, it can be seen that the mirex level for one site is very high, which is an obvious statistical outlier. It is the site 50m away from Guanghua Chemical Company and significantly influenced by the industrial activities nearby.

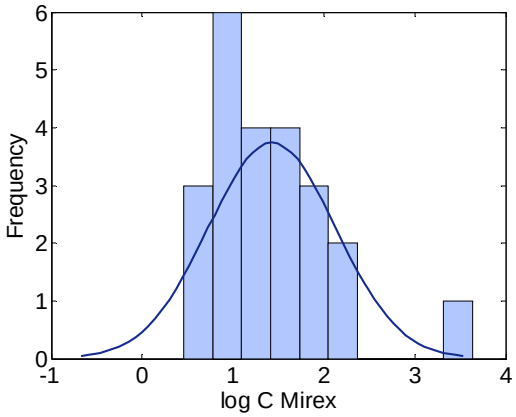

Fig. 3 The frequency distribution of mirex in soil in Liyang

Contour of mirex levels in soil in Liyang

The mirex levels obey the lognormal distribution, and the logarithm of concentrations of mirex were calculated and used for contour analysis (Fig. 4). From the contour map of mirex level in soil (Fig. 4), it can be seen that the Liyang Guanghua Chemical Company is the point pollution source with the highest mirex level. The Southern and Northwestern areas of the factory may be partially affected by the mirex transportation from the Liyang Guanghua Chemical Company because of the prevailing east wind in summer; and north wind in winter.

However, the influenced area and the extent to which it is influenced is rather limited.

Mirex pollution in Jiangsu province

Based on the model, the calculated mirex level in Jiangsu province is 18.06 pg/g in soil. If only the 16 sites (No. 1~ No. 16) were applied, the geometric mean of the detected mirex level was 13.55 pg/g in soil in Liyang. If the Site 23 (Liyang Guanghua chemical company) was not taken into consideration, the geometric mean was 21.30 pg/g for detected mirex in soil. The calculated mirex level in soil in Jiangsu province appropriated the statistical value of these observed values in Liyang, Jiangsu province. However, more data are needed for further validation. The total amount of mirex in the environment in Jiangsu is estimated to be about 460 kg. Most of the mirex existed in soil, accounting for more than 95% of the total amount of mirex. Mirex in the air and water is very limited.

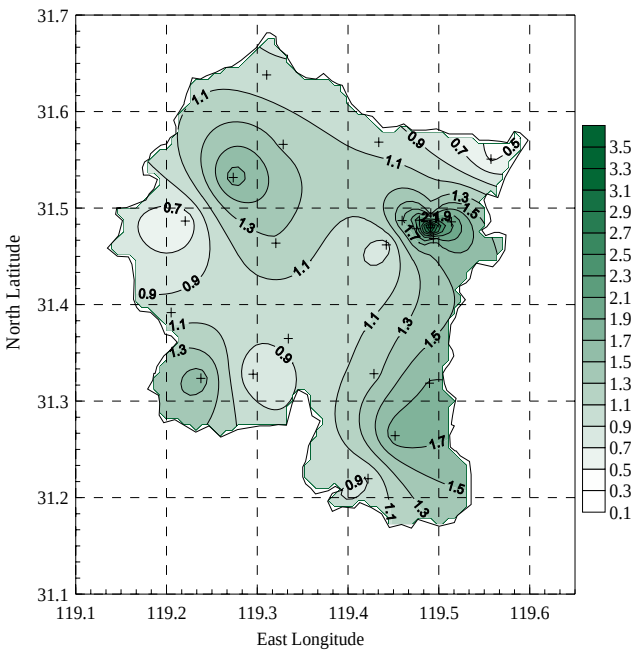

Fig. 4 Contour of mirex levels (log C_{Mirex}, pg/g) in the soil in Liyang (Kriging interpolation method was applied)

Acknowledgement

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