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Investigation of organochlorine pesticides (OCPs) in mollusks collected from coastal sites along the Chinese Bohai Sea from 2002 to 2004

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Concentration of organochlorine pesticides in mollusks collected from coastal sites along the Chinese Bohai Sea didn't change obviously from 2002 to 2004.

Abstract

Mollusks living in seas can accumulate organochlorine pesticides (OCPs). The residue levels of selected OCPs: dichlorodiphenyltrichloroethane (*p,p′*-DDT, *o,p′*-DDT, *p,p′*-DDE, *p,p′*-DDD), hexachlorocyclohexanes (α-, β-, γ- and δ-HCH) in gastropod and bivalve species collected from ten coastal cites along the Chinese Bohai Sea were investigated from 2002 to 2004. The species included nine kinds of mollusks: *Rapana venosa*, *Neverita didyma*, *Scapharca subcrenata*, *Mytilus edulis*, *Amusium*, *Crassostrea talienwhanensis*, *Meretix meretrix*, *Sinonovacula constricta*, *Ruditapes philippinarum*, *Mactra veneriformis*. The results showed that OCPs widely existed in the mollusks organisms. *p,p′*-DDT, *p,p′*-DDE, β-HCH were the major compounds. Statistical analysis (One-way ANOVA) showed that the contents of OCPs in these mollusks did not change obviously from 2002 to 2004. Principal component analysis (PCA) was also used for determining the polluting characters existing in this selected field.

Keywords: Mollusks; DDTs; HCHs; Principal component analysis; Bohai Sea

1. Introduction

Organochlorine pesticides (OCPs) are a common name of a group of pesticides consisting of benzene and chlorine, which have been of great of concern because of the large production and usage. Some OCPs belong to the Persistent Organic Pollutants (POPs) that are semi-volatile, environmental persistent, toxic. OCPs have bioaccumulation potential in organisms and long-term adverse effect on ecosystems and human health (Doong et al., 2002; Vallack et al., 1998; Jones and de Voogt, 1999). Considering to their harmful effects on human and ecosystem, during the last 30 years, many international agreements are coming into effect to reduce the environmental burden by reducing or withdrawing the registered usage of OCPs, for example, aldrin, diedrin, endrin, mirex, etc. But some of them, such as lindane (pure γ-HCH), are still used in some countries. In China, 1,2,3,4,5,6-hexachlorocyclohexane (HCHs), and dichlorodiphenyltrichloroethane (DDTs) were extensively used as pesticides for agricultural activities. Especially during 1960s to 1983, HCHs and DDTs accounting for about 78% of total pesticide production and usage (Hua and San, 1996; Li et al., 1998). Although the concentrations of OCPs in environmental matrix and foodstuffs have decreased since the 1980s because of the governmental restrictive measure, many studies showed the residues are still high (Nakata et al., 2002; Xu et al., 2004; Chen and Gao, 1993).

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Mollusks have been widely used to monitor the quality of water ecosystems since the late 1980s for their abundance in many terrestrial and aquatic ecosystems, being easily available for collection. They are highly tolerant to many pollutants and exhibit high accumulation property (Bervotes et al., 2005; Kim et al., 2002). Usually, the level of OCPs in organisms is relatively higher than those in the surrounding water. So, the analysis of OCPs in mollusks can help to monitor the quality of marine water and estimate the food safety risk for local people.

The Bohai Sea is a semi-enclosed coastal water body of Northwest Pacific. The coastal line of the Bohai Sea has a length of nearly 3800 km (Wei et al., 2002), with a surface area of 77×10^9 m^2. The Yellow River, Liaohe, Haihe and Luanhe (Fig. 1) are the major fresh water sources discharging directly to the Bohai Sea. The drainage areas of these rivers are the important agricultural and chemical production area.

The Bohai Strait in the east is the only passage connecting the Bohai Sea to the outer Yellow Sea. Once polluted, it needs a long period of time for water quality to resume.

In this study, nine widely distributed mollusk species were collected from ten sites around the Bohai Sea (37°30′–41°00′N latitude, 117°30′–121°30′E longitude). The main objectives are to investigate the residuals of HCHs and DDTs in the tissues of selected mollusks and evaluate the pollution levels of HCHs and DDTs in these sites.

2. Materials and methods

2.1. Sampling sites and samples collection

The sampling was carried out thrice from 2002 to 2004. The sampling period is from the end of July to the beginning of August in every year. Fig. 1 showed the map of the Bohai Sea and the sampling sites: Weihai, Yantai, Penglai, Laizhou, Yangkou, Tianjin, Huludao, Jinzhou, Yingkou, Dalian.

The species of selected mollusks (Table 1) were identified according to the catalog of marine mollusks in the reference book (Qi et al., 1989). The collected mollusks were depurated in filtered seawater for 24 h before transported to the laboratory with ice freezing. The soft tissues of mollusks were excised by stainless steel scalpel blades, and then thoroughly rinsed with Milli-Q water to remove extraneous impurities. After sufficient homogenate by a blender, the samples were kept at −20 °C until analysis.

Fig. 1. Sampling locations of mollusk samples along the Chinese Bohai Sea.

Table 1
The denomination of the selected mollusks

	Species	Abbreviate	Denomination
Gastropod (Predator)	*Rapana venosa*	Rap	Valenciennes, 1846
	Neverita didyma	Nev	Röding, 1798
Bivalve (Herbivore)	*Scapharca subcrenata*	Sca	Lischke, 1869
	Mytilus edulis	Myt	Linnaeus, 1758
	Amusium	Amu	Röding, 1798
	Crassostrea talienwhanensis	Cra (Ost)	Crosse, 1862
	Meretix meretrix	Mer	Linnaeus, 1758
	Sinonovacula constricta	Sin	Lamarck, 1818
	Ruditapes philippinarum	Rud	Adams & Reeve, 1850
	Mactra veneriformis	Mac	Reeve, 1854

2.2. Chemical analysis

2.2.1. Samples pretreatment

The pretreatment was modified according to the method by the work of Tanabe et al. (2000). Approximately 10 g (wet weight) homogenized soft tissues were added by appropriate anhydrous sodium sulfate, and mixed well using a glass rod. A suitable amount of internal standard (PCB-209, 0.2 μg mL^{-1}) was added. The mixtures then were extracted with sonication method by 80 mL 1:1 (v/v) hexane: dichloromethane for 60 min, then stood overnight. The extract was concentrated to about 1–2 mL. The concentrated extract was subjected to clean up by elution through a glass column (12 mm i.d.) filled with 10 g florisil. The analytes were eluted by 10 mL *n*-hexane and 30 mL 3:1 (v/v) *n*-hexane: dichloromethane in turn. The effluents were combined and the volume of samples was concentrated to about 1 mL by a gentle stream of nitrogen gas.

2.2.2. Standards, regents, and instrumental

The mixed OCPs standard solution including α-, β-, γ-, δ-HCH, *p,p′*-DDT, *o,p′*-DDT, *p,p′*-DDE, *p,p′*-DDD was purchased from National Research Center for Certified Reference Materials of China. The corresponding individual standards were also prepared for qualitative purpose. The internal standard 2,2′, 3,3′, 4,4′, 5,5′, 6,6′-decachlorobiphenyl was purchased from Accustandard, Inc. USA. All solvents were analytical-grade (Beijing Chemical Regents Factory, China).

The quantification of OCPs was performed by an Agilent 6890A gas chromatography (GC) equipped with a ^{63}Ni electron capture detector (micro-ECD) (Agilent, USA). A HP-1 fused-silica column (50 m × 0.25 mm i.d., 0.25 μm film thickness) was used for separation with high purity N_2 as the carrier gas and make-up gas at flow rate of 1 mL min^{-1} and 49 mL min^{-1}, respectively. The GC system was operated in a splitless mode and 1 μL of the extracts was injected through a programmable temperature vaporization (PTV). The oven temperature was raised from 80 °C to 200 °C at a rate of 10 °C/min, hold for 1 min, and then programmed to 270 °C at 5 °C/min, hold for 5 min. The injector and detector were maintained at 250 °C and 280 °C, respectively.

The residues of HCHs and DDTs were quantitatively determined by the calibration curves of the standards using peak areas. The quantitative determinations were performed be internal standard procedure. The quality assurance of analytical method could be found in our previous work (Yang et al., 2004).

2.3. Statistical analysis

Multivariate analysis method, principal component analysis (PCA) was used to extract of information from the chemical analysis of organisms (Hobbs