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Persistent Organochlorine Pesticides in River Waters of Southern Part of Okinawa Island, Japan

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Abstract: We investigated eight organochlorine pesticides (OCPs) in the rivers of southern part of Okinawa Island, Japan, from July to September 2005. The mean concentration for ΣBHC (α, β, γ, δ-BHC) in four rivers was 25.67 ± 58 ngL^{-1}(mean ± SD). The highest concentration of BHC detected in water samples was 49.10 ngL^{-1}. Other OCPs such as Aldrin, Dieldrin, Heptachlor epoxide (Isomer B) and Methoxychlor were also detected in most water samples with their mean concentrations of 6.96 ± 80, 4.33 ± 59.9, 3.16 ± 55 and 2.01 ± 57.6 ngL^{-1}. Within the monitoring period, the concentration of OCPs increases in July and August (Aldrin, α-BHC and β-BHC). The possible sources of these OCPs might be the effluents and dusts from residential areas and agricultural activities. The levels of OCPs in rivers in southern part of Okinawa were generally below the guideline values in Japan. This preliminary documentation of OCPs in river waters from southern part of Okinawa Island revealed that the rivers are lightly contaminated and suggesting more monitoring studies in order to protect the health of aquatic systems and accompanied life.

Key words: River waters, organochlorine pesticides, Okinawa Island.

Introduction

Organochlorine pesticides (OCPs) are organic compounds that to a varying degree resist photolytic, biological and chemical degradation. They are noted for their persistence and bioaccumulation characteristics. These compounds have been or continue to be used in large quantities and due to their environmental persistence they have the ability to bioaccumulate and biomagnify (Forget et al., 2002; Kennedy et al., 1998). Pesticide use has increased worldwide over the last four decades to an estimated 5.5×10^8 kg of active ingredient used in the United States and 2.59×10^9 kg used globally during 1995 (Golfinopoulos et al., 2002; Laabs et al., 2002) especially in tropical regions, agricultural intensification leading to higher consumption (Awofolu et al., 2003; Racke et al., 1997). Although it is undisputed that pesticides are essential in modern agriculture, there is growing concern about the toxic side effects of these chemicals that pose a potential threat to the environment. The presence of organochlorine pesticides (OCPs) in the environment has been of great concern due to their occurrence, persistence, toxicity in the environment and their bioaccumulation in humans and animals. Due to

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their widespread use, these compounds are detected by determination of their residues in various environmental matrices such as water, air, soil and biota (Zhang et al., 2002; Kang et al., 2001).

Several hundred pesticides of different chemical nature are currently used for agricultural purposes all over the world (Golfinopoulos et al., 2002). Pesticides are categorized into many classes of which the important are organochlorine and organophosphorus (Miliadis et al., 1993). Organochlorine pesticides (OCPs) are known to resist biodegradation and bioaccumulation in the environment. In fact many of these compounds are now classified as the so-called Persistent Organic Pollutants (POPs), because they can be recycled through food chains and produce a significant magnification of the original concentration at the end of the chain (Doong et al., 2002). OCPs residues reach the aquatic environment through direct run-off, leaching, equipment washing and careless disposal of empty containers to name a few (Nakai et al., 2004).

Some developing countries are still using chlorinated pesticides because of their low cost versatility in industry, agriculture and public health (Tanabe et al., 1994). In Japan, the using of these organochlorine pesticides has been prohibited in the field in the 1970s (Nakai et al., 2004). However, recent studies reconfirmed that OCPs residues are still environmentally persistent in nature (Nakai et al., 2004). In Vietnam, the prohibition of these substances was first issued in 1993, but some studies showed that DDTs were detected in their highest concentration (Hung and Thiemann, 2002). In Taiwan, a recent study showed that there still exists a variety of OCPs residues in the rivers wherein DDTs and HCHs were the dominant OCP compounds (Doong et al., 2002).

The rivers in the southern part of Okinawa provide habitat for the native fish such as Killifish (*Oryzias latipes*) and Paradise fish *(Macropodus opercularis)* which are now significantly thinning (Okinawa Prefecture Summary Plan, 2002). These rivers are vastly exposed to effluents from several sources such as domestic, agricultural, shipping and livestock farming (Sheikh et al., 2007). Nevertheless, information regarding the occurrence and the toxicological impacts of OCPs are very limited. The main objective of this study is to provide the information on the occurrence and behaviour of organochlorine pesticides in selected rivers located in the southern part of Okinawa Island, Japan.

Materials and Methods

Sampling

Water samples were collected from four rivers in the southern part of Okinawa Island during July-September 2005, as shown in Figure 1. Aja (Aj), Asato (As), Kokuba (Ko) and Houtoku (Ho) and six sampling points have been established for each river; starting from upstream and near the river banks in order to determine possible run-off of compounds from activities in the residential areas. Samples were taken using 2L glass bottles. The vials were carefully filled just to overflowing without passing air bubbles through sample or trapping air bubbles in sealed bottles. The vials were precleaned with soap, rinsed with ultrapure water (Milli Q plus 185) then with acetone and placed in the oven at 150°C for 1.5 hours. Samples were preserved by adding 5 mL of concentrated H_2SO_4 to avoid biological activity and were filtered using fibre-glass filters to remove debris and suspended material.

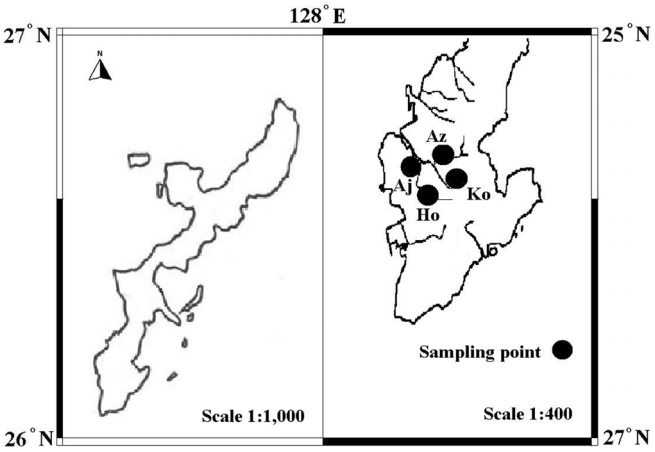

Figure 1: Map showing sampling locations in the Southern region of Okinawa Island, Japan.

Sample Extraction

The analytical procedure of OCPs in water samples was the modification of the method described by Hung and Thiemann (2002). The collected water samples were pre-filtered through 0.45 μm fiber glass filters to remove debris and suspended materials before being processed using a solid-phase extraction (SPE) technique. Methanol and Surrogate Standards (10 μgL^{-1}) were added to the one litre sample to allow better extraction (Chanel and Chang, 2002). Prior to the extractions, the Agilent SPE Cartridges (ENVI-18) were first conditioned with 5 mL

of methanol, 5 mL acetone and 5 mL of Milli Q water. The water samples of 20 mL were passed through the cartridges at a flow rate less than 10 mL/min. The cartridges were not allowed to become dry, as recommended by the Agilent SPE manual. The samples were well mixed and allowed to flow through the cartridges with a flow rate of 6-10 mL/min. Following extraction, the cartridges were eluted with 5 mL of acetone and 5 mL Milli Q water, and then centrifuged at 1000-1500 rpm for five minutes. The cartridges were eluted with 3 mL of acetone, and the dried extracts were collected and reduced to a volume of 2 mL under a gentle blow of dry nitrogen. One mL of the internal standard (pentachloronitrobenzene, 10 μgL^{-1}) was added to the vials before GC analysis.

Sample Analyses

The OCP residues were analyzed by Hewlett Packard Gas Chromatograph 6890 Plus, with a micro-cell electron capture detector (μECD), an autosampler and ChemStation software. A 30 m × 0.32 mm i.d. × 0.25 μm film thickness fused silica capillary column HP 1 was used for the chromatographic separation of pesticides. The oven temperature was programmed from 80°C to 190°C at 25°Cmin^{-1}, 190°– 280°C at 5°Cmin^{-1}, then 280–300°C at 25°Cmin^{-1} and held at 300°C for two minutes. Chlorinated pesticides standards (19 compounds each at 500 μgL^{-1}) and internal standard (pentachloronitrobenzene at 100 μL^{-1}) were obtained from AccuStandard. The stock solutions were diluted with ethyl acetate to prepare working standards which were later used to prepare calibration standards in the ranges of 0.1–25 μgL^{-1}. All solvents used for sample analyses (hexane, ethyl acetate, acetone) were of pesticide grade. The analytical quality control includes the analysis of blanks (Milli Q water), pre-extracted and spiked river water samples (10 μgL^{-1}) (n = 15) and duplicate analysis of samples from each sampling site shows good recoveries as shown in Table 1.

The gas chromatograms of OCPs standard and a sample are shown in Figures 2 and 3 respectively.

Table 1: Mean recovery (%), Relative standard deviation (%) and Limit of detection (LoD) for OCPs (n = 15)

Compound	*Recovery (%)*	*RSD (%)*	*LoD (ngL^{-1})*
Aldrin	74	20	0.12
α-BHC	70	11.1	0.23
β-BHC	88	12.8	0.06
γ-BHC (Lindane)	82	10	0.13
δ-BHC	84	15	0.04
Dieldrin	80	12.6	0.08
Heptachlor epoxide	73	14.3	0.03
Methoxychlor	75	15.8	0.59
Internal Standard	97	20.4	0.03

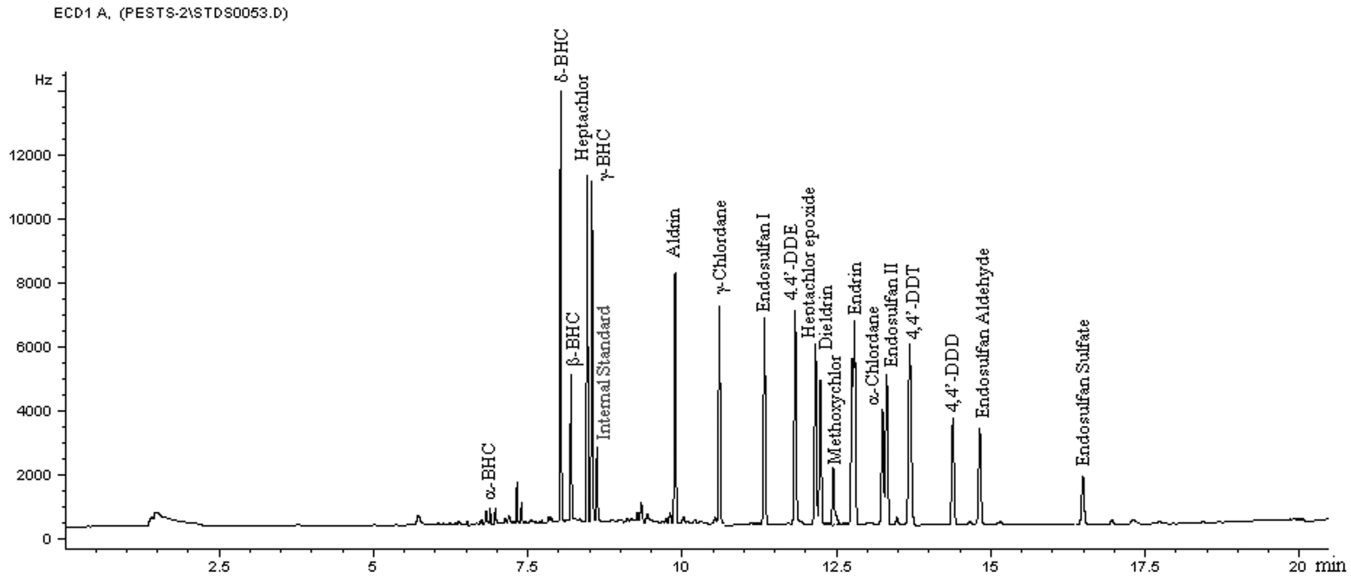

Figure 2: ECD Chromatogram of OCPs Standard.

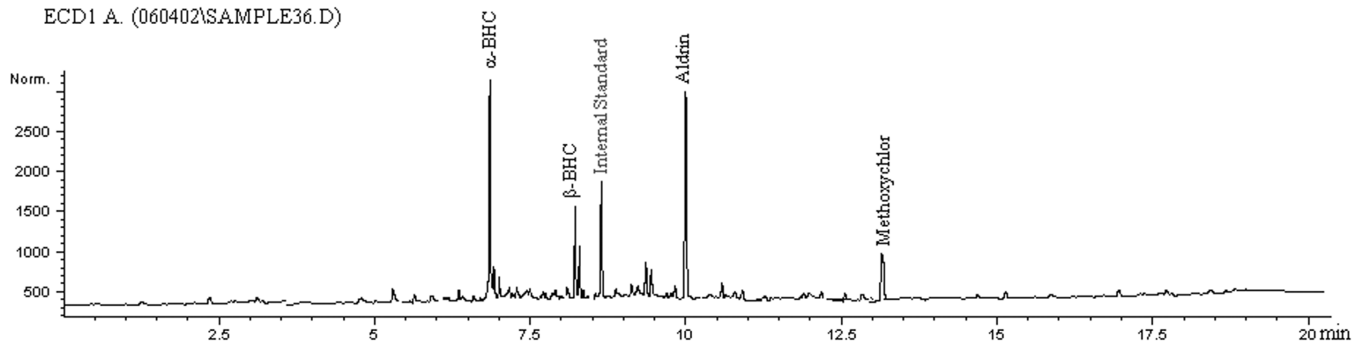

Figure 3: ECD Chromatogram of sample from Aja river, 2005.

Results and Discussion

The detected compounds were: Aldrin, α-BHC, β-BHC, γ-BHC, δ-BHC, Dieldrin, heptachlor epoxide (Isomer B) and methoxychlor. The OCPs concentrations detected in the surface waters of four rivers in southern Okinawa are shown in Table 2. The values shown in the table indicate the range of concentration during the period of

Table 2: Range of OCPs concentrations detected in the surface waters of four rivers in Southern Okinawa

Compound	*Concentration (ngL^{-1})*
Aldrin	<LoD – 29.50
α-BHC	<LoD – 49.10
β-BHC	<LoD – 18.40
γ-BHC (Lindane)	<LoD – 12.00
δ-BHC	<LoD – 8.01
Dieldrin	<LoD – 3.30
Heptachlor epoxide (Isomer B)	<LoD – 4.50
Methoxychlor	<LoD – 4.13

LoD: Limit of Detection

sampling from four rivers (July-September 2005). The OCPs concentrations from four rivers ranged from 3.80 ngL^{-1} to 49.10 ngL^{-1} with a mean concentration 24.21 ± 68.4 ngL^{-1}. The highest concentration of organochlorine pesticides were 29.50 ngL^{-1} (Aldrin), 49.10 ngL^{-1} (α-BHC), 18.40 ngL^{-1} (β-BHC), 12.00ng L^{-1} (γ-BHC), 8.01 ngL^{-1} (δ-BHC), 3.30 ngL^{-1} (Dieldrin), 4.50 ngL^{-1} (heptachlor epoxide) and 4.13 ngL^{-1} (Methoxychlor). The distribution of BHC isomers and other OCPs in river waters are shown in Figures 4 and Figure 5.

In Asato river, the highest concentration of OCPs was 49.10 ngL^{-1} (α-BHC) (July, 2005), followed by 29.50 ngL^{-1} (Aldrin) (July, 2005). The mean concentration of OCP for Asato river was 23.46 ± 68.6 ngL^{-1}; this could be due to the run-off effluents dust from residential areas or air circulation.

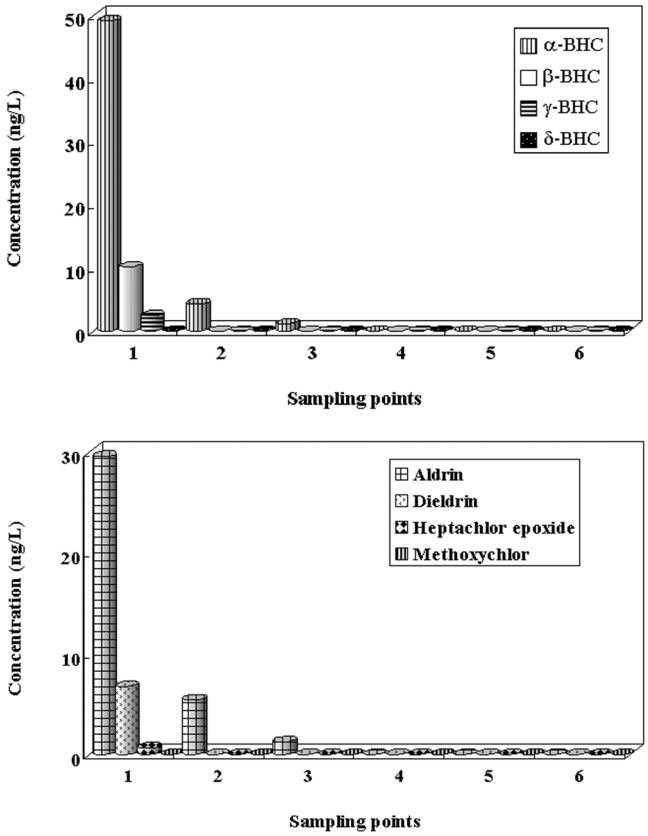

Figure 4: OCP concentration in Asato river collected in July, 2005.

The third highest OCPs concentration was found in Aja River; 18.40 ngL^{-1} (β-BHC) (August, 2005) followed by 12.00 ngL^{-1} (δ-BHC) (July, 2005). The mean concentration of OCPs for Aja river was 7.25 ± 72.6 ngL^{-1}. Aja river is also located within the residential area.

In Kokuba river, the highest OCPs concentration was 4.40 ngL^{-1} (α-BHC) (July, 2005), followed by 4.13 ngL^{-1} (α-BHC and β-BHC) (July, 2005). The mean concentration was 2.27 ± 59.3 ngL^{-1}. The least OCPs concentration was found in Houtoku river with 4.30 ngL^{-1} (Aldrin) (July, 2005) being the highest

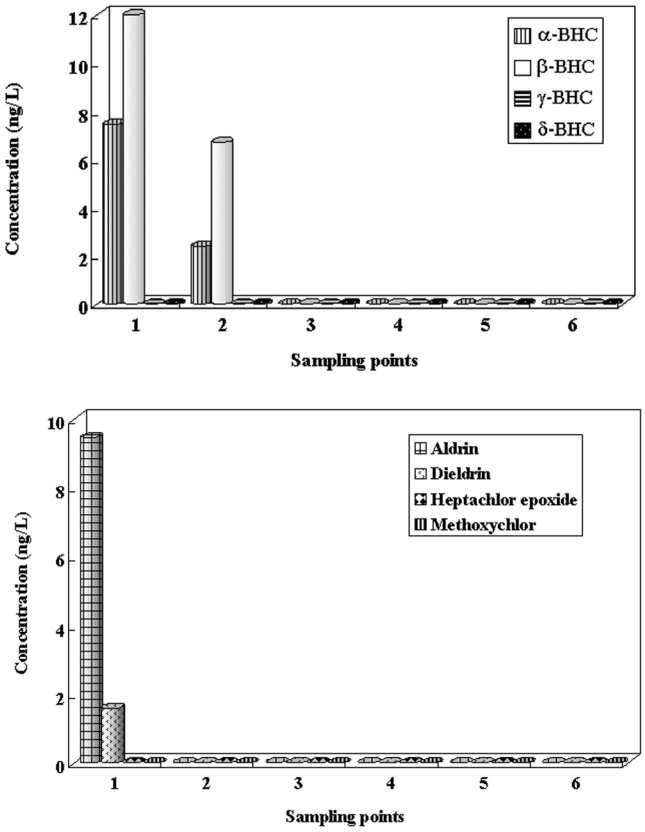

Figure 5: OCP concentration in Asato river collected in August, 2005.

concentration followed by 3.24 ngL^{-1} (α-BHC) (August, 2005). The mean concentration of OCPs was 2.18 ± 72.1 ngL^{-1}. It seems that within the five-month period, the concentration of OCPs increases in July and August (α-BHC, Aldrin and β-BHC) which means that most households use OCPs in the form of insecticides during these months.

It is suggested that the source of these OCPs in the surface waters comes from effluents dust of residential areas and leaching of water. As the input of pathways of OCPs into the river environment include run-off from non-point sources, leaching of water, and direct dumping of wastes into the river (Fushiwaki and Urano, 2001; Doong et al., 2002). The highest OCPs compounds, α-BHC, β-BHC and Aldrin, were the most detected OCPs compounds in all samples. In some samples, the concentrations of OCPs were lower than the qualitative target level set by the Japan Ministry of Environment and WHO, especially in the case of heptachlor epoxide and methoxychlor.

Conclusion

This survey provides the information on the current contamination status of four rivers located in the southern part of Okinawa Island. The OCPs which have been detected were Aldrin, α-BHC, β-BHC, δ-BHC, γ-BHC, Dieldrin, heptachlor epoxide and methoxychlor. Even though the concentrations of OCPs are comparatively lower, still the residues could be detected above the detection limit. The possible sources of these OCPs compounds could be from the dust and effluents from residential and agricultural areas. The levels of OCPs in the surveyed rivers may cause health impact on the aquatic environment and accompanied life. However, further monitoring studies are necessary to fully understand the behaviour and toxicological effects of OCPs to the aquatic environments.

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