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Distribution and risk assessment of suspected endocrine-disrupting pesticides in creek water of Mumbai, India

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ABSTRACT

The present study deals with the investigation of existing pollution levels and potential ecological risk assessment of endocrine-disrupting organochlorine and organophosphorous pesticide residues in the Vasai Creek water near Mumbai. The average concentration of α- and β-endosulfan (137.75 $ng \cdot L^{-1}$) exceeds the chronic criteria level of α- and β-endosulfan (6.5 $ng \cdot L^{-1}$) set by US EPA for freshwater aquatic organisms. The concentration levels of aldrin (75.31 $ng \cdot L^{-1}$), dieldrin (71.19 $ng \cdot L^{-1}$) and endrin (76.60 $ng \cdot L^{-1}$) was found to exceed the respective criteria levels of <0.13, 65.1, and 61 $ng \cdot L^{-1}$ as set by US EPA for protection of freshwater aquatic organisms. In addition, the level of chlorpyrifos (208.77 $ng \cdot L^{-1}$) exceeds the recommended concentration value of <35 $ng \cdot L^{-1}$ set by Ministry of Environment of British Colombia. The results of our study give an indication of probable ecotoxicological risk to the marine breeding organisms of creek.

1. Introduction

The existence of persistent organic pesticides in the environment and their threat to the wild life and mankind have raised a serious global concern. It is well known that DDT and other organic pollutants were listed by the Stockholm Convention in 2004 and in 2009, α-BHC, β-BHC, and γ-BHC (lindane) were newly added to the list (Hu et al., 2010). BHC and DDTs are ubiquitous chemicals and persistent, toxic and bioaccumulative in nature (Minh et al., 2006). They are responsible for acute as well as chronic effects on health leading to cancer, neurological damage, reproductive disorders, immune suppression, birth defects, and are also suspected endocrine disruptors (Van Den Berg et al. 2006; Wang et al., 2008; Mitra et al., 2011). Their physico-chemical properties like hydrophobicity and degradation resistance will result in accumulation of these chemicals not only in various environmental matrixes (Yang et al., 2005; Covaci et al. 2005; Kalantari and Ebadi, 2006; Hong et al., 2008; Wang et al., 2008; Musa et al., 2010) but also in human body through dietary intake, inhalation and other indirect exposure (Ebadi and Shokrzadeh, 2006; Alle et al., 2009). It is estimated that every year all over the world about 200,000 people die and around three million are poisoned due to pesticide pollution of which 95% of cases are from developing countries (WHO/UNEP, 1990; FAO/WHO, 2000; Pope et al, 1994). The sever effect of pesticides like DDT and BHC on human health is responsible for their restriction or ban in most of the countries (Jit et al., 2011; Van den Berg, 2009).

In spite of the ban on pesticides in India from 1985, DDT is still widely used in controlling of malaria (UNEP, 2003). Even though use of BHC is banned for use in agriculture, the government of India still permits the application of BHCs on specific crops and in health sector (Mukherjee and Gopal, 2003; Tanabe et al., 1994). Apart from India, there are some countries who are still engaged in large scale production, usage and export of γ-BHC (Abhilash and Singh, 2009). India is legally obligated to abide the objectives of the Stockholm Convention treaty and encouragement is given in order to support the research related to persistent organic pesticides in the environment. Due to tremendous increase in population coupled by heavy emphasis given in achieving food grain self-sufficiency has forced Indian farmers to continue with the regular use of pesticides. One estimate suggests that about 100,000 t of DDTs has been regularly used in India alone, mainly for use in agriculture and in programs related to the eradication of malaria (Yadav et al., 2015). This is mainly due to the low cost and broad-spectrum toxicity, which make them very efficient in controlling of pests and diseases (Kannan et al., 1995; Voldner and Li, 1995; Abhilash and Singh, 2009; Arora et al., 2013). Previous studies in India have revealed the contamination of various environmental matrices due to the accumulation of pesticides residues in biota and humans (Guzzella et al., 2005; Zhang et al. 2008; Chakraborty et al., 2010; Kumar et al., 2011a; Kumar et al., 2011b; Kumar et al., 2011c; Kumar et al., 2011d; Devi et al., 2011; Mukherjee et al., 2011; Pozo et al., 2011; Senthil Kumar et al., 2001; Mishra et al., 2008; Devanathan et al., 2008; Someya et al., 2009; Kumar and Mukherjee, 2012). The environmental contamination due to the pesticides is mainly due to their persistent and volatile nature

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and also due to atmospheric distribution through long range transportation (Bentzen et al., 2008; Caldas et al., 1999).

Although in India, extensive research work is performed on distribution of pesticide residues in different environmental matrixes, the work on distribution of these residues in aquatic environment is not given much attention. Despite of the importance of Vasai as evident from the previously published work (Singare, 2015; Singare, 2012; Singare et al., 2012a,b,c; Singare et al., 2011; Mehta and Amin, 2008; Lokhande and Kelkar, 1996a; Lokhande and Kelkar, 1996b), no systematic study was performed to understand the distribution of pesticide residues in the aquatic ecosystem. Hence, in the present paper attempts are made to address this deficit and present the results of a comprehensive survey of levels of organochlorine pesticides (OCPs) and organophosphate pesticides (OPPs) in the aquatic system of the Vasai Creek. The results of present study was compared with the level of pesticides in India water bodies which will help in understanding the current status of this contaminants and their probable ecotoxicological risk. It is no doubt that the distribution of these pesticides and their metabolites in the aquatic environment of Vasai Creek is of great significance in the context of global distribution and accumulation of these compounds.

2. Materials and method

2.1. Study site

The Ulhas Creek in Maharashtra state of western India splits at the northeast corner of Salsette Island into its two main distributaries, Vasai Creek and Thane Creek. Vasai Creek which is an estuarine creek that lies between latitude 19.315°N and longitude 72.875°E, forms the northern boundary of Salsette Island, and finally joins at the west into the Arabian Sea. The area experience subtropical climate, having mild winters and summers which are warm. The weather is typical coastal sultry and humid. The rainfall recorded here varies from average of 1500 mm to 2000 mm. The place experiences the onset of the monsoon in the month of June and experiences monsoon until the end of September. The temperature in the study area varies from 25 °C to 37 °C. The rapid urbanization and industrialization near the creek is responsible for discharge of domestic raw sewage as well as industrial waste water effluent in to the creek resulting in increased pollution level and change in physico-chemical properties of creek water (Singare et al., 2012a,b). Apart from the above factors, washing of cattle, clothes, and religious activities also contributes to the increase in pollution level of creek water (Singare, 2015; Singare, 2012; Singare et al., 2012a,b,c; Singare et al., 2011; Singare, 2012).

2.2. Water sampling and preservation

The collection of water samples was done monthly (n = 20 per sampling station per month) at an interval of every fifteen days for a span of two years starting from October 2009 to September 2011. The sampling was done in morning; afternoon and evening session randomly from sampling station S1 (Vasai Beach) and S2 (Bhayandar west side of Railway Bridge) along the Vasai Creek (Fig. 1). The sampling time in morning shift was between 07:00 a.m. and 09:00 a.m., in afternoon shift between 02:00 p.m. and 04:00 p.m. and evening shift between 07:00 p.m. and 09:00 p.m. The grab water samples were collected in 2.5 L and 2.0 L polythene bottles which were thoroughly cleaned with hydrochloric acid, washed with tape water to render free of acid, washed with distilled water twice, and again rinsed with the water sample to be collected. The bottles were then filled with the water sample leaving only a small air gap at the top. The sample bottles were stoppered and sealed with paraffin wax. The samples were kept cool in icebox during the transportation to the laboratory. Suspended particulate matter in the water samples were removed by filtering water samples through fluorine ethylene filters (50 mm × 0.45 mm, Millipore, USA). Water samples were taken using precleaned glass bottles and kept at −4 °C before extraction.

2.3. Extraction procedure

Water samples (1 L) were spiked with 20 ng of 2,4,5,6-tetrachloro-m-xylene (TCmX) and decachlorobiphenyl PCB209 and extracted three times with 25 mL dichloromethane each time. Activated copper granules were added to the collection flask to remove elemental sulfur. The extract of OCPs was concentrated and solvent-exchanged to n-hexane and further reduced to 2–3 mL by rotary evaporation. The alumina/silica ($v/v = 1:2$) gel column (both deactivated with three percent water) was used to purify the extract and OCPs were eluted with 30 mL of dichloromethane/hexane ($v/v = 2/3$). The solution thus eluted was concentrated to 0.2 mL under a gentle nitrogen stream. Before the analysis, known quantity of 3,3′,4,4′-tetrabromobiphenyl was added as an internal standard and then subjected to analysis by GC having electron capture detector.

During extraction of OPPs, 1 L of water samples was spiked with organophosphate standard solution by equilibrating in a separating funnel for 2 h (Tse et al., 2004). The OPP spike solution consisting of 1 $mg \cdot L^{-1}$ of a mixture of organophosphorous pesticide standards was prepared in acetone. The water samples were first filtered through a 125 mm filter (Fchleicher and Schuell 589.3, Germany) and then through a 0.5 μm glass microfiber filter (Rahmanikhah et al., 2010). The OPPs in the filtered water samples were extracted by solid-phase extraction using 6 mL Envir Elut PAH cartridges (Varian, U.S.A.). During extraction, the filtered samples were pumped at the rate of 10 mL/min into the cartridges. The cartridges were washed by elution with methanol and distilled water (Tariq et al., 2004). The care was taken to prevent the drying of cartridges (Albanis et al., 1998). The OPPs trapped in the cartridges were eluted by passing 10 mL of dichloromethane solvent (Albanis et al., 1998). The eluent was collected in 15 mL vials fitted with Teflon-lined caps having 1 g Na_2SO_4 which was added for dehydration (Sudo et al., 2002). The evaporation of solvent used for extraction of water sample was performed at 50 °C under the flow of nitrogen (Kammerbauer and Moncada, 1998; Sudo et al., 2002). Finally 0.3 mL of n-hexane was added to the vials in order to dissolve the remaining pesticide residues (Sudo et al., 2002; Sankaramakrishnan et al., 2004). The vials containing solution of dissolved pesticide residue were preserved at −15 °C to −20 °C (Sudo et al., 2002). For analysis, 1 μL of the extracted sample was injected in to the GC equipped with nitrogen–phosphorous detector (GC-NPD) (Sankaramakrishnan et al., 2004).

2.4. Analysis of pesticide residues

The Hewlett-Packard (HP) 5890A gas chromatograph model coupled with a ^{63}Ni electron capture detector, an on-column injector, and a HP-5MS fused silica capillary column (30 m, 0.32 mm, 0.25 μm) was used for analysis of OCPs. The temperature of detector was fixed at 315 °C. The temperature of oven was initially kept isothermal for 1 min at 100 °C, and then increased at a rate of 4 °C/min from 100 to 290 °C, the temperature was further kept isothermal at for 20 min at 290 °C. The carrier gas used was N_2 gas having 99.99% purity was made to flow at a rate of 1.0 mL/min under the constant flow mode. Before entering the gas chromatograph system, the carrier gas was made free of moisture, hydrocarbon and oxygen by passing through the filters. For analysis, 1 μL of the sample was injected. Analysis of OPPs was performed by using Hewlett-Packard (HP) 5890A gas chromatograph model coupled with nitrogen–phosphorous detector (NPD) having a fused silica capillary column (Optima 5 location) length of 6 m, 0.25 mm inner diameter and 0.25 μm film thickness. The helium gas having 99.000% purity as a carrier gas was made to flow rate at the rate of 3.6 mL/min. The temperature of injector and detector was fixed at 250 °C and 320 °C respectively. The temperature of oven temperature was kept at 90 °C for 1 min and then increased at a rate of 4 °C/min from

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