HISTORICAL TRENDS AND PROFILE PATTERNS OF PCDD/DFs AND DLPCBs IN YEONG-IL BAY CORE SEDIMENTS, KOREA

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Abstract

This study was carried out to investigation for historical trends, concentration profile and sources of PCDD/DFs and dioxin like-PCBs(DLPCBs) by using of sediment core samples at two site of A and B in Yeong-il Bay, Korea.
In the result of this study, the sediment core samples of 1940-1982 years (36-80cm) showed by stable period and the concentration of ΣPCDD/DFs ranged from 0.38 to 3.59 pg/g d.wt., while the toxic equivalence concentration of 17 congeners ranged from n.d to 1.03 pg WHO-TEQ/g d.wt. at site A. During the 1983-2005 year (surface-36 ㎝) that pollution of PCDD/DFs have been progressed and concentration of ΣPCDD/DFs was begin increasing from 1983yr by 45.75 pg/g d.wt., On 1997(14 - 16 ㎝) reached to maximum concentration of ΣPCDD/DFs by 1407.62 pg/g d.wt., While have been progressed begin decreasing from the 1999 yr(12-14cm).
In the case of Site B, time pick appeared of 2 times. The first time pick was estimated on 1945-1946 year (72-74 ㎝) and the concentration level was observed by 365.71 ng/g d.wt., while the second time pick was estimated on 1993s(18-20 ㎝) and maximum concentration was observed by 436.41 ng/g d.wt.

Introduction

It was investigated that historical trends, level and profile patterns of PCDD/DFs and PCBs have been used to the recognition and analyze their information for potential sources and pathway about environmental pollution of PCDD/DFs and PCBs, and using environmental media such biota, soils and sediments etc. [1-4]
Especially, After a study for PCDD/DFs by Czuczwa et al(1984) using sediment core samples ,which related research has been a lot of reported about temporal trend of PCDD/DFs and PCBs. [5-12]
By using sediment cores of northwestern of Balic Proper that profile patterns, concentration change and time trends of homologues and isomers for PCDD/DFs and PCBs were investigated by Lars-Owe Kjeller et al.,(1995).[6] In the results, the proposed sources were combustion of various natural items like coal, wood, and peat. Increased PCDD/DF and PCB levels were found during the period 1970-1985 by total PCDD/DFs 520-1800 pg/g. The main reason of pollution is indicated that the increased concentrations coincide with a change in PCDD/F congener profiles and isomeric patterns were by chloro-organics, and among them pentachlorophenol (PCP) one of the main contributors to PCDD/Fs.[6]
This study was carried out to investigation for historical trends, concentration profile and sources of PCDD/DFs and dioxin like-PCBs (DLPCBs) by using of sediment core in Yeong-il Bay, Korea.

Materials and Methods

Study area description is as following; Yeong-il Bay is the largest estuary on East-south coast in Korea. Fig.1 shows the study area of Yeong- il Bay which is quadrangle by open-end type and depth of about 20-30m, width of about 10km, length of about 13km, respectively. Also. Hyeongsan River water is flowing into the Bay, and industrial complex of steelworks exists.
Sediment core samples were collected at two sites on May, 2005 and shows to Fig.1 Sediment core samples were collected using core sampler of diameter 10 ㎝ x length 2m. Core samples did slice to 2 ㎝ thickness, and make 40 slice in each core sample and obtained all 80samples. Sediment core samples were refrigerated and frozen until use at -70℃, and removed water by freeze dryer. Sediment core samples were homogenized and Soxhlet extracted for 24h using toluene (Ultra residue analysis, J.T.Baker) and concentrated using a rotary evaporator.

Extract solutions were concentrated using nitrogen gas after add n-Nonane (Pesticide residue analysis, Fluka) 500μL by keeping solvent, and changed solvent by n-Hexane(Ultra residue analysis, J.T.Baker) and finally internal standard (EDF-8999 및 EC-4977) were spiked in 10ml n-Hexane solution samples.
Clean-up of extracts samples were carried out multi layer silica-gel and activated alumina column chromatography. The samples were analyzed according to congener group of the PCDD/DFs by HRGC/HRMS(HP 6890 GC coupled to a JEOL JMS-700D HRMS). Detailed descriptions of the clean-up, fractionation procedures and instrumental analysis have been presented elsewhere (Ok et al., 1998).[14]

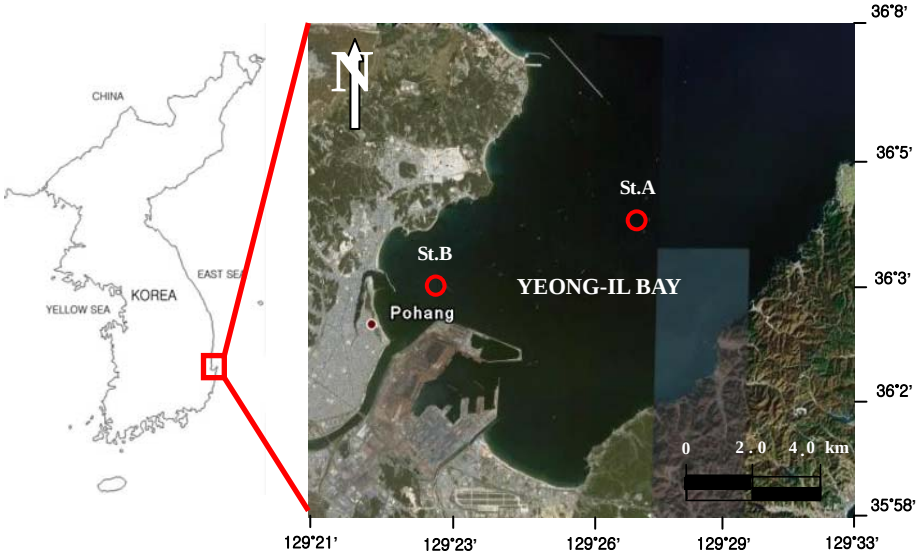

Fig. 1. Map of the Yeong-il Bay and sediment core samples collection site.

Results and Discussion

Fig.2 shows the concentration levels of historical time trends and profile patterns of PCDD/DFs and DLPCBs to sediment core samples at two site of A in Yeong-il Bay, Korea.
In the result of this study, the sediment core samples of 1940-1982 years (36-80cm) showed by stable period and the concentration of ΣPCDD/DFs ranged from 0.38 to 3.59 pg/g d.wt., while the toxic equivalence concentration of 17 congeners ranged from n.d to 1.03 pg WHO-TEQ/g d.wt. at site A. During the 1983-2005 year (surface-36 ㎝) that pollution of PCDD/DFs have been progressed and concentration of ΣPCDD/DFs was begin increasing from 1983yr by 45.75 pg/g d.wt., On 1997(14 - 16 ㎝) reached to maximum concentration of ΣPCDD/DFs by 1407.62 pg/g d.wt., While have been progressed begin decreasing from the 1999 yr (12-14cm).
Historical time trend and concentration trend of this results are coincide with studied which is reported in order to compare in the Southern Sea, Western Sea and East Sea of Korea for PCDD/DFs by Ok et al.,[13], so that time, PCDD/DFs' concentration was observed by highest level in Yeong-il Bay. On the other hand, at this point this time, also impose legal controls on PCDD/DFs was begun time in Korea.
In the case of Site B, time pick appeared of 2 times, and ΣPCDD/DFs' concentration range was 2.83 - 436.41 ng/g d.wt. The first time pick was estimated on 1945-1946 year (72-74 ㎝) and the concentration level was observed by 365.71 ng/g d.wt., while the second time pick was estimated on 1993s(18-20 ㎝) and maximum concentration was observed by 436.41 ng/g d.wt. But, 2,3,7,8-substituted WHO-TEQ concentration was observed in the first time pick by maximum concentration. This reason was consideration that TEQ concentration was dominated by 2, 3, 7, 8 - TCDDs concentration as well as other low chlorination compounds, also, contribution rate was showed higher by low chlorination compounds in profile patterns. According to the result origin by the two time picks are considered to be different.
When the homologue profile pattern was observed time pick of the 1940s at site B, the contribution of

concentration was confirmed higher low chlorinated PCDD/DFs rather than high chlorinated PCDD/DFs. This result can be assumed that origin is a low temperature more than occurrence profile pattern by high temperature.
In this study, sedimentation velocity was calculated at site A and B by 1.58 cm/s and 1.48 cm/s, and accumulate rate was estimated at site A and B by 0.79 g/cm^2/year and 0.74 g/cm^2/year, respectively.
After 1992, profile pattern of sediment core for PCDD/DFs was similar with Hyeongsang Rive water, and loading of inflow can presume for one of origination from Hyeongsang River. Also, relativity with operation time of surrounding steel industrial facilities was assumed by historical time trend of PCDD/DFs concentration in sediment core.

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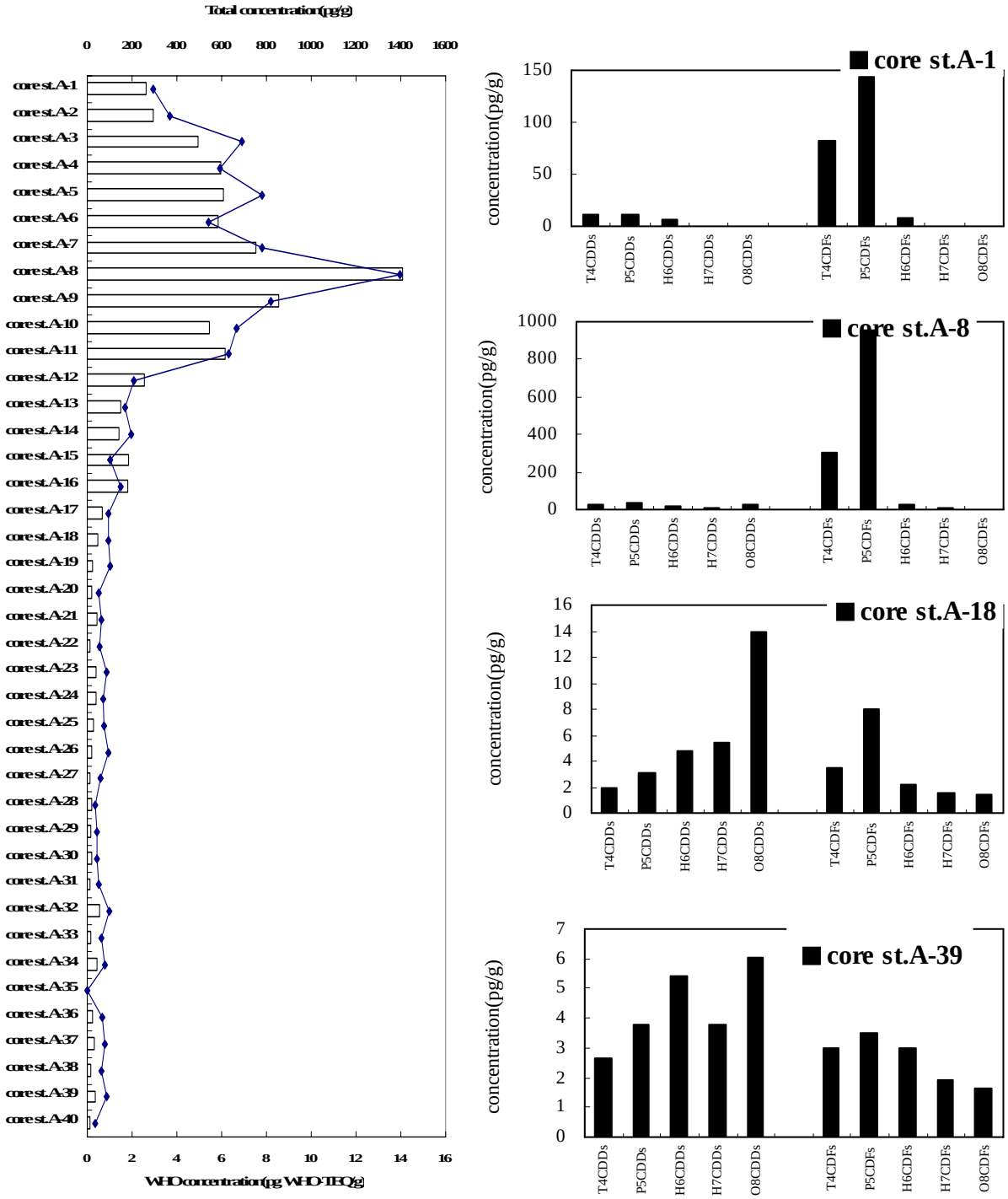

Fig.2.Historical time trends, concentration levels and profile patterns of PCDD/DFs to sediment core samples at site A in Yeong-il Bay, Korea.