

DETERMINATION OF LOW DIOXINS AND PCB'S CONCENTRATION IN AMBIENT WATER USING LARGE VOLUME "IN SITU" PRE-CONCENTRATION SYSTEM

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Introduction

Determination of the concentration and congener and/or isomer distributions for PCDDs/PCDFs and PCBs in ambient water is indispensable for tracing the fate of these compounds and to assess the risk to biological organisms. However, very few reports regarding water media have been done because of low concentrations of PCDDs/PCDFs and PCBs.

A large volume "*In situ*" pre-concentration system for ambient water sampling was developed for the determination of ultra low concentrations of PCDDs/PCDFs and PCBs in ambient water, and used to sample river water and tap water.

Description of Sampler

Figure 1 shows a schematic diagram of the "*in situ*" pre-concentration system. The housing is constructed of electrolyze-mirror polish treated stainless steel (SUS), and encloses the air removal chamber (ARC), a glass fiber filter (GFF) holder, polyurethane form plug (PUFP) holders, valves, sensors with an external computer controller.

Water samples pass through the ARC to remove air bubbles in water to prevent air from reaching the water-bypass in the GFF or PUFPs. After the removal of air bubbles, sample passes through the GFF filter (300mm ID, 0.5 μ m pore size), PUFP (100mm ID, 100mm height) and back-up PUFP (100mm ID, 100mm height). A flow rate sensor monitors the flow rate of sample and maintains a constant sampling rate. The computer controls the needle valve based on information from the sensors. After sampling is completed, shutdown valves mounted on an entrance and an exit of the line are closed to protect the samples from contamination. Valves, sensor, air removal chamber, GFF holder and PUFP holder are enclosed in a SUS box to prevent atmospheric contamination.

The system design makes it possible to sample m^3 of water at the flow rate of 1-2L/min (=60-120L/hrs =1440-2880L/day). Using this system, the concentration of PCDDs/PCDFs and co-planer PCBs in ambient water samples was determined.

Sampling

The “*in situ*” pre-concentration system was applied to several water samples. 100-200L and 1500-2000L of river and tap water samples were collected, respectively. Flow rates were controlled within 2.0mL/min/PUFP bed volume cm^3 .

Analysis

Detection of PCDDs/PCDFs and co-planer PCBs was carried out by HRGC/HRMS method after soxhlet extraction and gel clean-up procedures.

GFF and PUFPs were dried in a desiccator. After spiking with internal standard ^{13}C compounds, PCDDs/PCDFs and co-PCBs, PUFP were extracted by methylene chloride for 24hrs, GFF using toluene for (24hrs) with a soxhlet extractor. Multi layer silica gel and activated carbon column chromatographies were employed for sample clean up. Concentration of PCDDs, PCDFs and co-PCBs were determined by of isotope dilution HRGC (6890, Hewlett Packard, US)/HRMS (AutoSpec-Ultima, Micromass, UK). Seventeen native and ^{13}C 2,3,7,8- substituted dioxin/furan isomers (Wellington Laboratories, Canada) and twelve native (IUPAC #77, #81, #126, #169, #105, #114, #118, #123, #156, #157, #167, and #189) (AccuStandard, USA) and ^{13}C (Wellington Laboratories, Canada) co-PCBs were used as internal and isotope spike standards.

Organic solvents used for analysis were purified by non-boiling distillations. Glassware, GFF and SUS were heated to 300°C after an organic solvent wash. PUFPs were pre-washed by soxhlet (methylene chloride, >24hrs) after a water and acetone wash. All procedures were carried out in a clean room (class<10000).

BPX-5 (60m length, 0.25 mm ID, 0.25 μm film thickness, SGE, Australia) and a BPX-50 (60m length, 0.25 mm ID, 0.25 μm film thickness, SGE, Australia) are equipped for HRGC to reduce the chemical background from liquid phase.

Results and Discussion

Large volume sampling, low sampling/reagents/operation blank value and high sensitivity GC-MS operations make low detection limits possible. An example of results is shown in *Table 1*. In this study, detection limits achieved for each compound are about 0.001-0.02pg/L. A TEQ detection limit of 0.0025pg-TEQ/L (2000L sampling) was achieved

As an example of results, congener distribution for particulate (trapped by GFF) and dissolved (trapped by PUFP) constituents of river water are shown in *Figure 2* and *3*. Particulate fraction represents a low percent of total concentration of PCDDs/PCDFs (*Figure 2*), and dissolved fraction was decreased from tetra to octa (*Figure 3*). These results represent suitable recognition of the physicochemical properties of PCDDs/PCDFs, such as water solubility and adsorption properties.

Using this system it is possible to detect low pg/L concentrations of PCDDs, PCDFs and PCBs in ambient water at levels of interest.

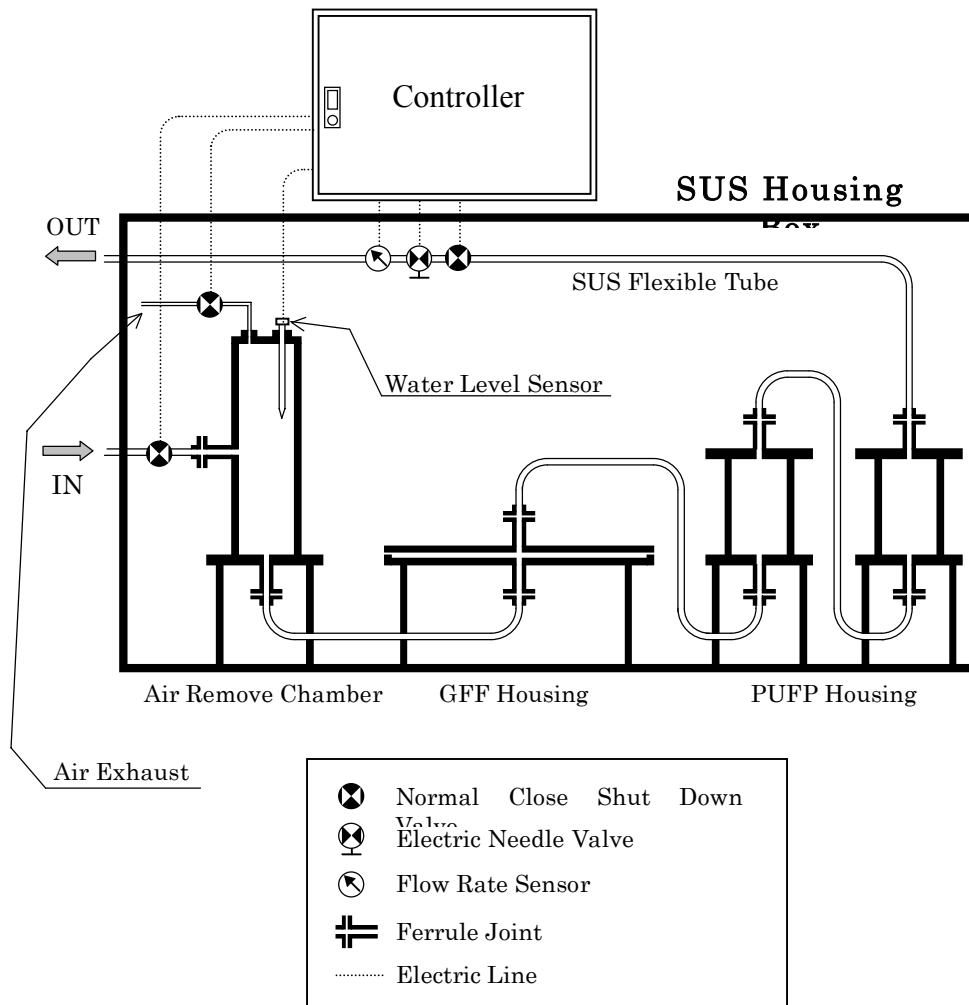


Figure 1. Schematic diagram of large volume "in situ" pre-concentration system.

Table 1. Example of result for PCDDs, PCDFs and co-PCBs in particulate fraction for river water.

Compound	IUPAC No.	Measured (pg/L)	WHO, 1997-TEF		
			TEF	TEQ (pg-TEQ/L)	
P C D D s	1,3,6,8-TeCDD	-	1.3	-	-
	1,3,7,9-TeCDD	-	0.51	-	-
	2,3,7,8-TeCDD	-	0.004	1	0.004 ₀₀
	TeCDDs	-	2.7	-	-
	1,2,3,7,8-PeCDD	-	0.019	1	0.019 ₀
	PeCDDs	-	0.67	-	-
	1,2,3,4,7,8-HxCDD	-	<0.002	0.1	0 (<0.0001 ₀₀)
	1,2,3,6,7,8-HxCDD	-	0.058	0.1	0.0058 ₀
	1,2,3,7,8,9-HxCDD	-	0.046	0.1	0.0046 ₀
	HxCDDs	-	0.60	-	-
	1,2,3,4,6,7,8-HpCDD	-	1.1	0.01	0.011 ₀
	HpCDDs	-	2.5	-	-
	OCDD	-	17	0.0001	0.0017 ₀
	Total PCDDs	-	24	-	0.051 ₉ (<0.049 ₇)
P C D F s	1,2,7,8-TeCDF	-	0.028	-	-
	2,3,7,8-TeCDF	-	0.030	0.1	0.0030 ₀
	TeCDFs	-	0.42	-	-
	1,2,3,7,8-PeCDF	-	0.029	0.1	0.0014 ₅
	2,3,4,7,8-PeCDF	-	0.041	0.5	0.020 ₅
	PeCDFs	-	0.37	-	-
	1,2,3,4,7,8-HxCDF	-	0.047	0.1	0.0047 ₀
	1,2,3,6,7,8-HxCDF	-	0.042	0.1	0.0042 ₀
	1,2,3,7,8,9-HxCDF	-	<0.002	0.1	0 (<0.0001 ₀₀)
	2,3,4,6,7,8-HxCDF	-	0.087	0.1	0.0087 ₀
	HxCDFs	-	0.50	-	-
	1,2,3,4,6,7,8-HpCDF	-	0.31	0.01	0.0031 ₀
	1,2,3,4,7,8,9-HpCDF	-	0.050	0.01	0.00050 ₀
	HpCDFs	-	0.69	-	-
OCDF	-	0.39	0.0001	0.000039 ₀	
Total PCDFs	-	2.4	-	0.046 ₂ (<0.046 ₃)	
Total (PCDDs+PCDFs)	-	26	-	0.092 ₃ (<0.092 ₅)	
C o P C B s	3,3',4,4'-TeCB	(#77)	1.4	0.0001	0.00014 ₀
	3,4,4',5'-TeCB	(#81)	0.05	0.0001	0.000005 ₀₀
	3,3',4,4',5'-PeCB	(#126)	<0.02	0.1	0 (<0.0002 ₀₀)
	3,3',4,4',5',5'-HxCB	(#169)	<0.02	0.01	0 (<0.00002 ₀₀)
	non-ortho PCBs	-	1.5	-	0.00014 ₅ (<0.00036 ₅)
	2,3,3',4,4'-PeCB	(#105)	4.0	0.0001	0.00040 ₀
	2,3,4,4',5'-PeCB	(#114)	0.32	0.0005	0.00016 ₀
	2,3',4,4',5'-PeCB	(#118)	13	0.0001	0.0013 ₀
	2',3,4,4',5'-PeCB	(#123)	0.28	0.0001	0.000028 ₀
	2,3,3',4,4',5'-HxCB	(#156)	2.1	0.0005	0.0010 ₅
	2,3,3',4,4',5',5'-HxCB	(#157)	<0.02	0.0005	0 (<0.000001 ₀₀)
	2,3',4,4',5',5'-HxCB	(#167)	0.91	0.00001	0.0000091 ₀
	2,3,3',4,4',5,5'-HpCB	(#189)	0.091	0.0001	0.0000091 ₀
mono-ortho PCBs	-	20	-	0.0029 ₆ (<0.0029 ₇)	
Total Co-PCBs	-	22	-	0.0031 ₀ (<0.0033 ₂)	
Total (PCDDs+PCDFs+Co-PCBs)	-	-	-	0.095 (<0.096)	

