DEVELOPMENT OF AIR PRECIPITATION TRAP SAMPLER FOR DIOXINS

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Introduction

Precipitation from air (wet/dry fallout) is one of the most important "Flux" to trace the environmental fate and/or behavior of dioxins. In general, precipitation is trapped in cylindrical vessels or deposit cages. However, due to re-scattering of collected particles and decomposition (dechlorination for organohalogen compounds) of compounds by sunlight and/or re-volatilization of collected compounds, these sampling methods are not suitable to estimate the "Flux" of organic compounds. These phenomena result in an under-estimation of compounds' "Flux". In addition, because dechlorination rates of each dioxin congener is different, congener and isomer distributions observed might differ from actual distributions patterns at the time of collection.

An air precipitation trap sampler was developed in order to obtain more accurate data regarding "Flux" of dioxins from air to land.

Description of Sampler

Figure 1 shows a schematic diagram of the "Automated Air Precipitation Trap Sampler". The main apparatus is constructed of mirror polished stainless steal (SUS). The system includes a glass fiber filter (GFF) holder, polyurethane form plug (PUFP) holder, water pump, valves, heater, sensors, and a computer controller. Key characteristics are listed below.

(1)Air precipitation (rain, snow, dust, etc.) fall into circulating water in the sampling vessel.
(2)Sample is carried from vessel by water circulated by a pump.
(3)Particulate matter in the sample is trapped by a GFF (150mm ID, 0.5µm pore size) in a GFF holder.
(4)Dissolved constituents are then trapped by a PUFP (100mm ID, 100mm height) in a PUFP holder.
(5)Water is returned to sampling vessel. (Water is swirled in the sampling vessel to reduce residence time.)
(6)Computer controlled vessel cover is moved depending on weather conditions (wet(rain)/dry(fine), day/night, wind direction, atmospheric stability…..).
(7)Electronic level sensors monitor water level in the vessels. If water level increase, water is discharge via a bypass. If water level decrease, water is added from a water reservoir.
(8)Water temperature is monitored by a sensor. At the water temperature below 5ºC, vessel, GFF holder, PUFP holder and SUS tube are heated to prevent freezing.
(9)Information of regarding cover position is record into data logger together with date and time.

Experiment

Four types of sampling vessels (*Figure 2*) were made to compare the sampling efficiency. Inner walls of all vessels were constructed of mirror polished SUS.

Type-A: Cylindrical vessel.
Type-B: Same as the Type-A, but water added in the vessel (water depth = 50mm).
Type-C: Funnel-shaped vessel.
Type-D: Same as *Figure-1*, however, in this comparison experiment, the fractionation mechanism was not used.

These four types of vessels were placed on top of a building for 10 days. Vessel Types-C was rinsed with water several times during sampling period.

Analysis

Detection of PCDDs/PCDFs 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 were extracted by methylene chloride (24hrs) using soxhlet extraction. Multi layer silica gel and activated carbon column chromatographies were employed for sample clean up. Concentration of PCDDs, PCDFs were determined by of isotope dilution HRGC (6890, Hewlett Packard, US)/HRMS (AutoSpec-Ultima, Micromass, UK). Seventeen native (Wellington Laboratories, Canada) and [13]C 2,3,7,8-substituted isomers (Wellington Laboratories, Canada) were used as standard and isotope spike.

Organic solvents used in analysis were purified by non-boiling distillations. Glassware, GFF and SUS were heated to 300ºC after organic solvent wash. PUFPs were pre-washed by soxhlet (methylene chloride, >24hrs) after water and acetone wash.

Results and Discussion

Results are shown in *Table 1*. There are large differences between the duplicate results for the Type-A. A likely reason is re-scattering of trapped particulate. The smaller difference between duplicate values for the Type-C compared to the Type-A may be due to the effect of water rinse during the sampling period. Duplicate results for the Type-B and the Type-D were in good agreement, probably due to particulate being trapped by water. However, there were significant differences in the absolute values of the Type-B and the Type-D. There is a distinct possibility of decomposition and/or dechlorination of dioxins in water by sunlight irradiation. An additional possibility is the volatilization of dioxins for the Type-B.

Congener profiles were different for each type of vessel. For example, ratios of PCDFs/PCDDs are shown in the bottom row of *Table 1*. The values for the Type-A, B and C are significantly smaller than that of the Type-D. It is thought that this phenomenon is caused by differing rates of decomposition, dechlorination and/or volatilization for each dioxin congener.

Using this type of sampler, it is possible to assess the accurate "Flux" of organohalogen compounds from air to land at levels of interest.
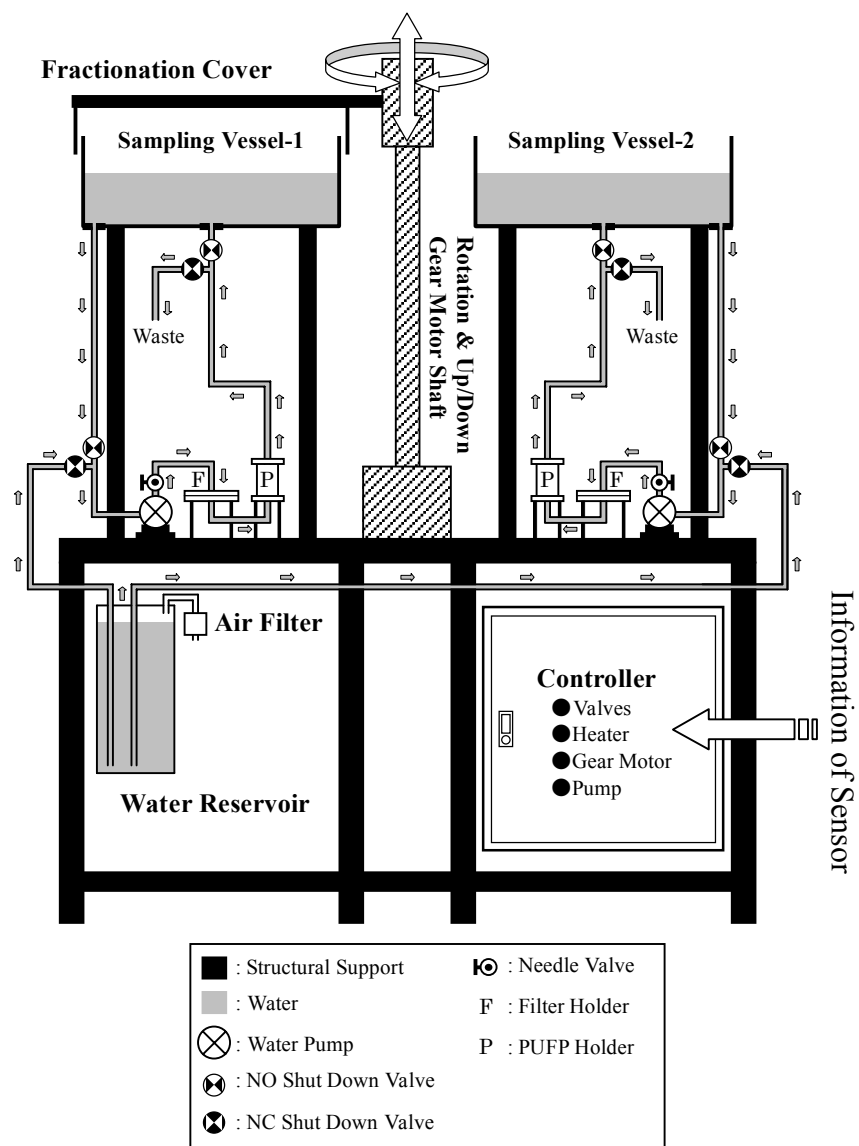
Figure 1. Schematic diagram of "Automated Air Precipitation Trap Sampler" (Type-D).
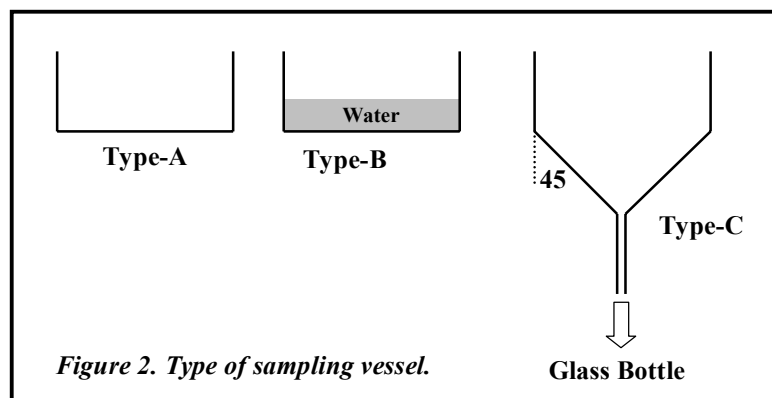
Figure 2. Type of sampling vessel.

Table 1.   Congener concentrations and TEQs obtained by 4 types of samplers. Superscript numbers are to distinguish between duplicate sampling/analysis.

(unit : $pg/m^2/day$)

Congener	Type of Sampler							
	A^1	A^2	B^1	B^2	C^1	C^2	D^1	D^2
TeCDDs	27	8	17	15	21	10	69	83
PeCDDs	27	11	22	24	32	16	67	57
HxCDDs	100	25	56	54	59	47	120	89
HpCDDs	110	39	100	90	110	80	170	140
OCDD	340	140	340	270	490	340	630	660
PCDDs	600	220	540	450	710	490	1100	1000
TeCDFs	44	17	40	37	62	24	200	210
PeCDFs	51	20	35	39	67	42	130	130
HxCDFs	110	26	56	50	90	62	150	150
HpCDFs	46	14	40	34	70	55	120	110
OCDF	18	8	19	13	30	21	60	67
PCDFs	270	85	190	170	320	200	660	670
PCDDs+PCDFs	870	310	730	630	1000	700	1700	1700
TEQ	13	3.3	6.3	5.4	8.7	5.9	16	15
Ratio of PCDFs/PCDDs	0.45	0.39	0.35	0.38	0.45	0.41	0.60	0.67