ENVIRONMENTAL LEVELS OF DECHLORANE PLUS IN JAPAN: HOW TO CONTROL THE ACCURACY OF ANALYSIS

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Introduction

Dechlorane Plus (DP) was developed as a chlorinated flame retardant to replace Mirex (Dechlorane) which was banned in the 1970s, and detection has increased rapidly in Europe and China in recent years. However, since there has been no report in Japan, we have conducted research on domestic environmental pollution using GC/EI-MS analysis. As a result, DP has been detected for the first time from environmental samples collected from urban regions in Japan.

The concentration levels of DP ranged from 2.9-42ng/g-dry in indoor dust, 240-270ng/g-dry in dust adhering to windowsills, 74-150ng/g-dry in street dust, 1.7ng/g-dry in soil and 17-140ng/g-dry in sediment. Also, the ratio of *anti* formation isomers (f_{anti}) of DP were 0.65, 0.83, 0.80, 0.81 and 0.81, respectively. In this research, the concentration and f_{anti} ratio of DP in indoor dust, soil, and sediment were levels comparable to the reports from other countries.

Moreover, we reported procedures necessary and important to control the accuracy of DP analysis. It is necessary to pay attention for solvent dilution and temperature and stock concentration since we verified that the *anti* level decreases if we store a standard solution of 100 ug/mL of *n*-nonane at -25ºC during the research.

Further research on the actual status of DP pollution in this country to ascertain the cause of pollution is needed.

Materials and methods

Native and ^{13}C labeled standard solutions of Dechlorane Plus (DP) and Mirex (Dechlorane) were purchased from Cambridge Isotope Laboratories, Inc (CIL). High purity (Chromatography grade) organic solvents were used in sample treatment and standard dilution.

Sample treatment and GC/MS measurement followed previously described method[1)] (Fig.1). Details can be found in Table 1.

Results and discussion

[Measurement]

In GC/MS analysis for DP, the sensitivity decreases due to formation of a large number of fragment ions by using EI. Thus, NCI is usually used, but it is believed that detecting DP is possible even by EI because DP is detected in higher than ng/g level in the environment samples in most cases. However, since ions of ^{13}C labeled and unlabeled overlap when using low-resolution GC/MS, it may be difficult to adopt isotope dilution using ^{13}C labeled standards.

[Validation of analysis]

Native standard solution of two Dechlorane Plus (DP) isomers (*anti* and *syn*) and corresponding ^{13}C labeled isomers were used in this research.

Firstly, DP native standard solutions (100ug/mL in Nonane) were stored in a freezer at -25°C within a sealed ampoule for about 1 and a half year. Those were removed and allowed to reach room temperature for half a day. The samples were not vortexed or sonicated. A portion of those solutions was measured. The measured peak intensity of the *anti* isomer was only about 20-30% of that of the *syn* isomer (Fig.2). For the solution stored at room temperature, the ratio of the *anti* isomer was not decreased (Table2). Compared with the solution from the same batch stored at room temperature, the concentration of *anti* only in low temperature was low. This phenomenon applied to solutions of both ^{13}C labeled and unlabeled DP. However, we could not confirm these changes in solutions of DP (10ug/mL in Nonane) stored in a freezer at -25°C for about 1 month.

While decrease of the concentration of *anti*-DP in Nonane solutions has been reported by Torre, his report also says this has not been applied to solutions of Toluene in low-temperature preservation. But no concentration has so far been reported for the solutions when reduction in the concentration of *anti* was determined.

In this case, we suggest that decrease of the concentration of *anti*-DP may possibly be not only attributable to kinds of solvents for dilution, but also depends on the concentration of solutions. Therefore, careful attention should be paid to concentration along with solvents for dilution and storage temperature on the DP analysis.

[Environmental levels]

The comparison of a measurement result on DP with other studies is given in Fig.3. Quantification by the isotope dilution technique found the concentration level of DP in environmental samples (sediment, soil, dust *etc*.) in Japan ranged from 1.7 to 270ng/g-dry (Fig.3).

Acknowledgements

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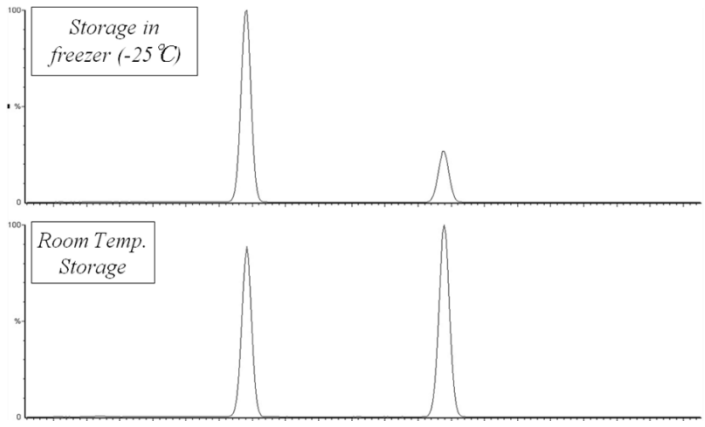


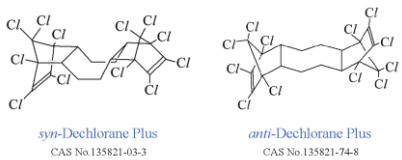


Fig. 2 Peak area comparision of Anti- and Syn-DP

Table 1. GC/MS Measurement Condition for Dechlorane Plus and Mirex(Dechlorane).

【GC Condition】

GC System	: Agilent 6890
Column	: HT8-PCB (Kanto Chemical Co.,Inc, Length:60m, I.D.:0.25mm)
Injection Mode	: Split less (Purge on :1.0min)
Injectoin Temperature	: 290℃
Carrier Gas, Column Flow	: Helium, 1.0mL/min (Constant Flow Mode)
Oven Temperature	: 120 ℃ (2min) - 20 ℃/min - 180 ℃ - 2 ℃/min - - 250 ℃ - 20 ℃/min - 340 ℃ (Hold)

【MS Condition】

MS System	: Micromass Autospec Ultima		
Ionizatin Mode	: EI		
Ion Source Temperature	: 290℃		
Monitor Ion			
	Native	: 271.8102	, 273.8072
	^{13}C Labeled	: 276.8269	, 278.8240
	Syringe Spike	: 303.9597	, 301.9626
	Lock Mass (PFK)	: 292.9824	
GC Retention Time(min)			
	Syringe Spike	: 26.22	
	Mirex(Dechlorane)	: 42.17	
	syn -Dechlorane Plus	: 53.89	
	anti -Dechlorane Plus	: 54.86	

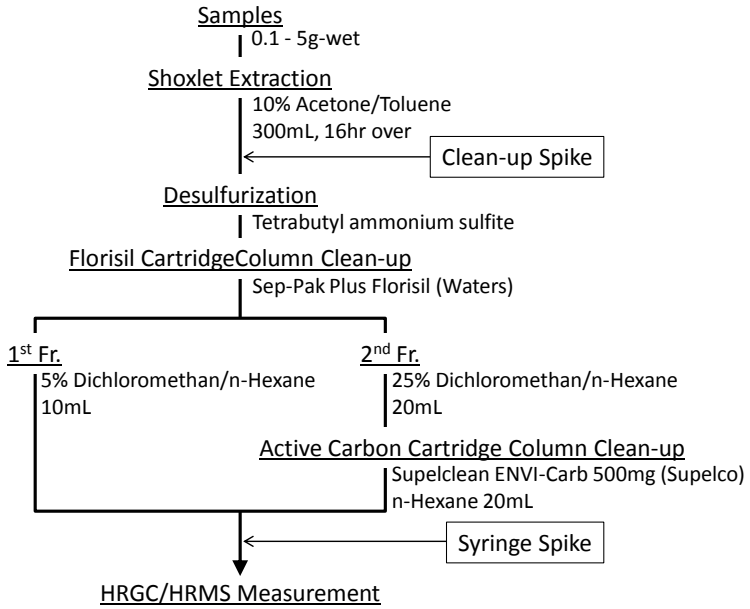
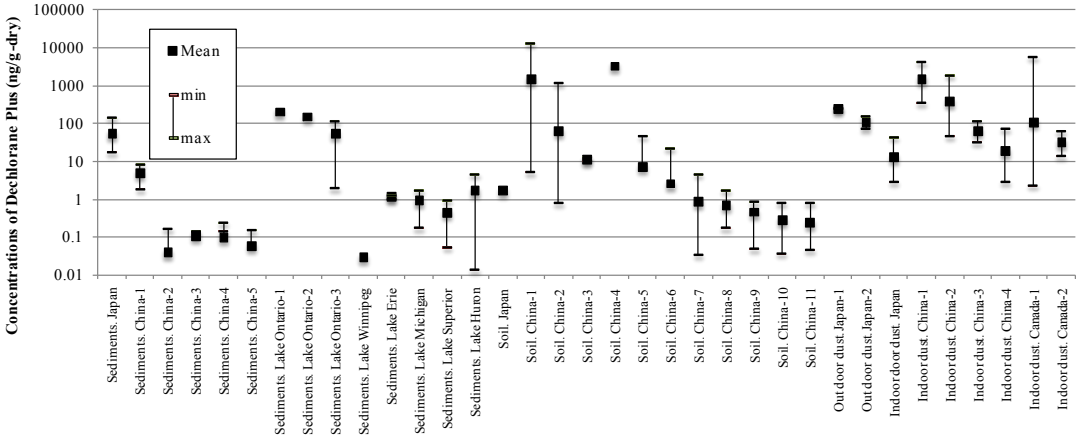


Fig. 1



Sample Lavels	Sampling location	Number of sample	Sampling year	Ref.
Sediments. Japan	**Urban rivers, Osaka**	**4**	**2008, 2010**	**3)**
Sediments. China-1	Canal in DP production facility, Huai-An	2	2009	4)
Sediments. China-2	Songhua River, Rural area	18	2006	5)
Sediments. China-3	Songhua River, Urban area, Harbin City	4	2006	5)
Sediments. China-4	Songhua River, Urban area, Harbin City	3	2007	6)
Sediments. China-5	Urban river, Harbin City	6	2006	5)
Sediments. Lake Ontario-1	Lake Ontario	3	1998	7)
Sediments. Lake Ontario-2	Lake Ontario	1	2006	8)
Sediments. Lake Ontario-3	Lake Ontario	6	2006, 2007	9)
Sediments. Lake Winnipeg	Lake Winnipeg	4	2000-2003	7)
Sediments. Lake Erie	Lake Erie	2	2004	9)
Sediments. Lake Michigan	Lake Michigan	2	2002	9)
Sediments. Lake Superior	Lake Superior	6	2001	9)
Sediments. Lake Huron	Lake Huron	8	2002	9)
Out door dust. Japan-1	**Deposits of window, Urban area,**	**2**	**2011**	**3)**
Out door dust. Japan-2	**Road sediments, Urban area, Osaka**	**2**	**2011**	**3)**

Sample Lavels	Sampling location	Number of sample	Sampling year	Ref.
Soil. Japan	**Urban area, Home garden, Osaka**	**1**	**2011**	**3)**
Soil. China-1	Near DP production facility, Huai-An	15	2009	4)
Soil. China-2	Around DP production facility, Huai-An	21	2009	10)
Soil. China-3	Urban area, Harbin	3	2007	6)
Soil. China-4	E-waste recycling site, Qingyuan	1	2004	11)
Soil. China-5	Around e-waste recycling site, Qingyuan	26	2004	11)
Soil. China-6	Industrial regions, Guiyu	23	2004	11)
Soil. China-7	Industrial regions, Foshan	8	2004	11)
Soil. China-8	Industrial regions, Dongguan	6	2004	11)
Soil. China-9	Industrial regions, Jiangmen	2	2004	11)
Soil. China-10	Industrial regions, Zhongshan	9	2004	11)
Soil. China-11	Industrial regions, Zhuhai	5	2004	11)
Indoor door dust. Japan	**Residential homes, Urban area, Osaka and Hyogo**	**5**	**2011**	**3)**
Indoor dust. China-1	Workshop, E-waste recycling site, Longtang Town	13	-	12)
Indoor dust. China-2	Residental homes, E-waste recycling site, Longtang	10	-	12)
Indoor dust. China-3	Residental homes, Rural area, Yuantan Town	10	-	12)
Indoor dust. China-4	Residental homes, Urban area, Guangzhou City	27	-	12)
Indoor dust. Canada-1	Residental homes, Urban area, Ottawa	69	2002-2003	13)
Indoor dust. Canada-2	Residental homes, Urban area, Ottawa	7	2007	13)

Fig.3 Levels of Dechlorane Plus in Various Environmental Samples

Table 2. Effect of the storage temperature on Anti-DP concentration

Sample	Temp.	Room temp.			-25℃		
	solvent	n-Nonane			n-Nonane		
	conc. (μg/mL)	100			100		
		Unlabeled DP			Unlabeled DP	$^{13}C_{10}$ labeled DP	
Dilution	solvent	n-Nonane		50% nonane in toluene	n-Nonane	n-Nonane	50% nonane in toluene
	conc. (μg/mL)	0.5	1	0.5	0.5	1	0.5	0.5
Mean of peak area ratio (anti/syn)		1.25	1.30	1.20	0.30	0.29	0.34	0.35