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Global and selective detection of organohalogens in environmental samples by comprehensive two-dimensional gas chromatography–tandem mass spectrometry and high-resolution time-of-flight mass spectrometry

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ABSTRACT

We successfully detected halogenated compounds from several kinds of environmental samples by using a comprehensive two-dimensional gas chromatograph coupled with a tandem mass spectrometer (GC × GC–MS/MS). For the global detection of organohalogens, fly ash sample extracts were directly measured without any cleanup process. The global and selective detection of halogenated compounds was achieved by neutral loss scans of chlorine, bromine and/or fluorine using an MS/MS. It was also possible to search for and identify compounds using two-dimensional mass chromatograms and mass profiles obtained from measurements of the same sample with a GC × GC-high resolution time-of-flight mass spectrometer (HRTofMS) under the same conditions as those used for the GC × GC–MS/MS. In this study, novel software tools were also developed to help find target (halogenated) compounds in the data provided by a GC × GC-HRTofMS. As a result, many dioxin and polychlorinated biphenyl congeners and many other halogenated compounds were found in fly ash extract and sediment samples. By extracting the desired information, which concerned organohalogens in this study, from huge quantities of data with the GC × GC-HRTofMS, we reveal the possibility of realizing the total global detection of compounds with one GC measurement of a sample without any pre-treatment.

1. Introduction

As the number of environmental pollutants increases, they become increasingly expensive in terms of the time and cost needed to monitor and count them. This can be partly attributed to problems with analytical methods, which require a lot of time and resources, and where a skilled user is needed to measure trace levels of compounds precisely in the presence of a large amount of interference, and because the methods are individually optimized for each target substance. We are improving and developing methods and tools to overcome the problems related to the methods used for analyzing organic environmental pollutants.

Global detection, which can be used to search for a large number of substances simultaneously, namely, non-target analysis, is one approach for addressing the increasingly diverse range of environmental pollutants. The direct measurement of samples without any compound loss is ideal for the complete global detection of pollutants. However, a conventional gas chromatograph (GC), which is a mainstream tool for analyzing environmental pollutants, cannot separate the huge number of compounds contained in a crude sample. In recent years, comprehensive two-dimensional gas chromatography (GC × GC), which is a high performance technique for the separation of chemical compounds, has been used to characterize hundreds or perhaps thousands of petroleum chemicals [1–3] as well as food components and flavors [4–6]. GC × GC technology has also been used to analyze environmental contaminants with many congeners such as polychlorinated biphenyls (PCBs) [7–12], polybrominated diphenyl ethers (PBDEs) [9,12,13], toxaphene [14], polyaromatic hydrocarbons (PAHs) [7,15,16], and other halogenated compounds [9,10] as well as polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/Fs) [17–19]. In our recent studies, we quantified dioxins in extracts of fly ash and flue gas samples [20] without employing any cleanup process by using a GC × GC connected to a high resolution time-of-flight mass spectrometer (HRTofMS). Moreover, PCBs and persistent organic pollutants (POPs) collected in a Tenax-TA tube from only 3 to 4 m^3

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Table 1
List of standard organohalogens used for measurement in this study.

Compound name	Abbrev	Concentration (ng/ml)	ID[a]	RT on 1st GC (min)	RT on 2nd GC (s)
Dioxins					
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin	2378TCDD	200	D2	24.406	2.309
1,2,3,7,8-Pentachlorodibenzo-*p*-dioxin	12378PeCDD	1000	D3	27.939	2.237
1,2,3,4,7,8-Hexachlorodibenzo-*p*-dioxin	123478HxCDD	1000	D4	30.739	2.525
1,2,3,6,7,8-Hexachlorodibenzo-*p*-dioxin	123678HxCDD	1000	D5	30.873	2.453
1,2,3,7,8,9-Hexachlorodibenzo-*p*-dioxin	123789HxCDD	1000	D6	30.939	2.309
1,2,3,4,7,8,9-Heptachlorodibenzo-*p*-dioxin	1234678HpCDD	1000	D7	33.673	2.453
Octachlorodibenzo-*p*-dioxin	OCDD	2000	D8	36.339	3.752
2,3,7,8-Tetrachlorodibenzofuran	2378TCDF	200	F1	23.939	2.525
1,2,3,7,8-Pentachlorodibenzofuran	12378PeCDF	1000	F2	26.939	2.381
2,3,4,7,8-Oentachlorodibenzofuran	23478PeCDF	1000	F3	27.739	2.453
1,2,3,4,7,8-Hexachlorodibenzofuran	123478HxCDF	1000	F4	30.139	2.381
1,2,3,6,7,8-Hexachlorodibenzofuran	123678HxCDF	1000	F5	30.206	2.453
1,2,3,7,8,9-Hexachlorodibenzofuran	123789HxCDF	1000	F6	31.206	2.381
2,3,4,6,7,8-Hexachlorodibenzofuran	234678HxCDF	1000	F7	31.473	2.742
1,2,3,4,6,7,8-Heptachlorodibenzofuran	1234678HpCDF	1000	F8	32.739	2.381
1,2,3,4,7,8,9-Heptachlorodibenzofuran	1234789HpCDF	1000	F9	34.139	2.886
Octachlorodibenzofuran	OCDF	2000	F10	36.539	0.144
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin [$^{13}C_{12}$]	2378TCDD-L	100	(D2)		
1,2,3,7,8-Pentachlorodibenzo-*p*-dioxin [$^{13}C_{12}$]	12378PeCDD-L	100	(D3)		
1,2,3,4,7,8-Hexachlorodibenzo-*p*-dioxin [$^{13}C_{12}$]	123478HxCDD-L	100	(D4)		
1,2,3,6,7,8-Hexachlorodibenzo-*p*-dioxin [$^{13}C_{12}$]	123678HxCDD-L	100	(D5)		
1,2,3,7,8,9-Hexachlorodibenzo-*p*-dioxin [$^{13}C_{12}$]	123789HxCDD-L	100	(D6)		
1,2,3,4,6,7,8-Heptachlorodibenzo-*p*-dioxin [$^{13}C_{12}$]	1234678HpCDD-L	100	(D7)		
Octachlorodibenzo-*p*-dioxin [$^{13}C_{12}$]	OCDD-L	200	(D8)		
2,3,7,8-Tetrachlorodibenzofuran [$^{13}C_{12}$]	2378TCDF-L	100	(F1)		
1,2,3,7,8-Pentachlorodibenzofuran [$^{13}C_{12}$]	12378PeCDF-L	100	(F2)		
2,3,4,7,8-Pentachlorodibenzofuran [$^{13}C_{12}$]	23478PeCDF-L	100	(F3)		
1,2,3,4,7,8-Hexachlorodibenzofuran [$^{13}C_{12}$]	123478HxCDF-L	100	(F4)		
1,2,3,6,7,8-Hexachlorodibenzofuran [$^{13}C_{12}$]	123678HxCDF-L	100	(F5)		
1,2,3,7,8,9-Hexachlorodibenzofuran [$^{13}C_{12}$]	123789HxCDF-L	100	(F6)		
2,3,4,6,7,8-Hexachlorodibenzofuran [$^{13}C_{12}$]	234678HxCDF-L	100	(F7)		
1,2,3,4,6,7,8-Heptachlorodibenzofuran [$^{13}C_{12}$]	1234678HpCDF-L	100	(F8)		
1,2,3,4,7,8,9-Heptachlorodibenzofuran [$^{13}C_{12}$]	1234789HpCDF-L	100	(F9)		
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin [$^{37}Cl_4$]	2378TCDD-L2	200	(D2)		
1,2,3,4-Tetrachlorodibenzo-*p*-dioxin [$^{13}C_{12}$]	1234TCDD-L	100	D1	24.073	2.381
POPs					
Hexachlorobenzene	HCB	800	P2	13.205	722
Alpha-hexacyclohexane	a-HCH	800	P1	13.005	0.866
Beta-hexacyclohexane	b-HCH	800	P4	13.805	1.227
Gamma-hexacyclohexane	g-HCH	800	P3	13.605	1.371
Delta-hexacyclohexane	d-HCH	800	P5	14.472	1.804
Heptachlor	HpCHL	800	P6	15.938	1.227
cis-Heptachlor epoxide	c-HpEPO	800	P9	18.605	2.02
trans-Heptachlor epoxide	t-HpEPO	800	P10	18.805	2.093
cis-Nonachlor	c-NoCHL	800	P19	22.805	2.165
trans-Nonachlor	t-NoCHL	800	P14	20.205	1.804
cis-Chlordane	c-CHL	800	P13	20.072	2.165
trans-Chlordane	t-CHL	800	P11	19.538	2.02
Oxychlordane	OxyCHL	800	P8	18.538	1.732
2,4′-DDD	opDDD	800	P17	21.272	2.598
4,4′-DDD	ppDDD	800	P21	22.938	2.381
2,4′-DDE	opDDE	800	P12	19.605	2.381
4,4′-DDE	ppDDE	800	P15	20.938	2.237
2,4′-DDT	opDDT	800	P20	22.805	2.453
4,4′-DDT	ppDDT	800	P22	24.405	2.309
Aldrin	ALD	800	P7	17.205	1.443
Dieldrin	DLD	800	P16	21.272	2.237
Endrin	END	800	P18	22.205	2.526
Mi rex	MRX	800	P23	28.605	2.309
Hexachlorobenzene [$^{13}C_6$]	HCB-L	20	(P2)		
Alpha-HCH [$^{13}C_6$]	a-HCH-L	20	(P1)		
Beta-HCH [$^{13}C_6$]	b-HCH-L	20	(P4)		
Gamma-HCH [$^{13}C_6$]	g-HCH-L	20	(P3)		
Delta-HCH [$^{13}C_6$]	d-HCH-L	20	(P5)		
Heptachlor [$^{13}C_{10}$]	HpCHL-L	20	(P6)		
cis-Heptachlor epoxide [$^{13}C_{10}$]	c-HpEPO-L	20	(P9)		
cis-Nonachlor [$^{13}C_{10}$]	c-NoCHL-L	20	(P19)		
trans-Chlordane [$^{13}C_{10}$]	t-CHL-L	20	(P11)		
Oxychlordane [$^{13}C_{10}$]	OxyCHL-L	20	(P8)		
2,4′-DDD [$^{13}C_{12}$]	opDDD-L	20	(P17)		
4,4′-DDD [$^{13}C_{12}$]	ppDDD-L	20	(P21)		
2,4′-DDE [$^{13}C_{12}$]	opDDE-L	20	(P12)		
4,4′-DDE [$^{13}C_{12}$]	ppDDE-L	20	(P15)		
2,4′-DDT [$^{13}C_{12}$]	opDDT-L	20	(P20)		
4,4′-DDT [$^{13}C_{12}$]	ppDDT-L	20	(P22)		

Table 1 (*Continued*)

Compound name	Abbrev	Concentration (ng/ml)	ID[a]	RT on 1st GC (min)	RT on 2nd GC (s)
Aldrin [$^{13}C_{12}$]	ALD-L	20	(P7)		
Dieldrin [$^{13}C_{12}$]	DLD-L	20	(P16)		
Endrin [$^{13}C_{12}$]	END-L	20	(P18)		
Mirex [$^{13}C_{10}$]	MRX-L	20	(P23)		
PCBs					
2-Chlorobiphenyl	PCB1	400	B1	11.272	0.289
4-Chlorobiphenyl	PCB3	400	B2	11.938	0.433
2,2′-Dichlorobiphenyl	PCB4	400	B3	12.338	0.649
4,4′-Dichlorobiphenyl	PCB15	400	B6	14.338	1.155
2,2′,6-Trichlorobiphenyl	PCB19	400	B5	13.605	1.082
3,4,4′-Trichlorobiphenyl	PCB37	400	B11	17.605	2.02
2,2′,6,6′-Tetrachlorobiphenyl	PCB54	400	B7	15.072	1.66
3,3′,4,4′-Tetrachlorobiphenyl	PCB77	400	B16	21.472	2.453
3,4,4′,5-Tetrachlorobiphenyl	PCB81	400	B15	21.072	2.381
2,2′,4,6,6′-Pentachlorobiphenyl	PCB104	400	B10	17.238	1.804
2,3,3′,4,4′-Pentachlorobiphenyl	PCB105	400	B21	23.538	2.526
2,3,4,4′,5-Pentachlorobiphenyl	PCB114	400	B19	22.938	2.381
2,3′,4,4′,5-Pentachlorobiphenyl	PCB118	400	B18	22.472	2.237
2′,3,4,4′,5-Pentachlorobiphenyl	PCB123	400	B17	22.338	2.237
3,3′,4,4′,5-Pentachlorobiphenyl	PCB126	400	B24	24.938	2.309
2,2′,4,4′,6,6′-Hexachlorobiphenyl	PCB155	400	B12	19.405	1.948
2,3,3′,4,4′,5-Hexachlorobiphenyl	PCB156	400	B27	26.538	2.309
2,3,3′,4,4′,5′-Hexachlorobiphenyl	PCB157	400	B28	26.738	2.381
2,3′,4,4′,5,5′-Hexachlorobiphenyl	PCB167	400	B25	25.672	2.093
3,3′,4,4′,5,5′-Hexachlorobiphenyl	PCB169	400	B29	28.005	2.165
2,2′,3,4′,5,6,6′-Heptachlorobiphenyl	PCB188	400	B20	23.005	2.093
2,3,3′,4,4′,5,5′-Heptachlorobiphenyl	PCB189	400	B30	29.338	2.237
2,2′,3,3′,5,5′,6,6′-Octachlorobiphenyl	PCB202	400	B26	26.205	2.02
2,3,3′,4,4′,5,5′,6-Octachlorobiphenyl	PCB205	400	B33	30.672	2.237
2,2′,3,3′,4,4′,5,5′,6-Nonachlorobiphenyl	PCB206	400	B34	31.738	2.309
2,2′,3,3′,4,5,5′,6,6′-Nonachlorobiphenyl	PCB208	400	B31	29.672	2.165
Decachlorobiphenyl	PCB209	400	B35	37.738	2.309
2-Chlorobiphenyl [$^{13}C_{12}$]	PCB1-L	100	(B1)		
4-chlorobiphenyl [$^{13}C_{12}$]	PCB3-L	100	(B2)		
2,2′-Dichlorobiphenyl [$^{13}C_{12}$]	PCB4-L	100	(B3)		
4,4′-Dichlorobiphenyl [$^{13}C_{12}$]	PCB15-L	100	(B6)		
2,2′,6-Trichlorobiphenyl [$^{13}C_{12}$]	PCB19-L	100	(B5)		
3,4,4′-Trichlorobiphenyl [$^{13}C_{12}$]	PCB37-L	100	(B11)		
2,2′,6,6′-Tetrachlorobiphenyl [$^{13}C_{12}$]	PCB54-L	100	(B7)		
3,3′,4,4′-Tetrachlorobiphenyl [$^{13}C_{12}$]	PCB77-L	100	(B16)		
3,4,4′,5-Tetrachlorobiphenyl [$^{13}C_{12}$]	PCB81-L	100	(B15)		
2,2′,4,6,6′-Pentachlorobiphenyl [$^{13}C_{12}$]	PCB104-L	100	(B10)		
2,3,3′,4,4′-Pentachlorobiphenyl [$^{13}C_{12}$]	PCB105-L	100	(B21)		
2,3,4,4′,5-Pentachlorobiphenyl [$^{13}C_{12}$]	PCB114-L	100	(B19)		
2,3′,4,4′,5-Pentachlorobiphenyl [$^{13}C_{12}$]	PCB118-L	100	(B18)		
2′,3,4,4′,5-Pentachlorobiphenyl [$^{13}C_{12}$]	PCB123-L	100	(B17)		
3,3′,4,4′,5-Pentachlorobiphenyl [$^{13}C_{12}$]	PCB126-L	100	(B24)		
2,2′,4,4′,6,6′-Hexachlorobiphenyl [$^{13}C_{12}$]	PCB155-L	100	(B12)		
2,3,3′,4,4′,5-Hexachlorobiphenyl [$^{13}C_{12}$]	PCB156-L	100	(B27)		
2,3,3′,4,4′,5′-Hexachlorobiphenyl [$^{13}C_{12}$]	PCB157-L	100	(B28)		
2,3′,4,4′,5,5′-Hexachlorobiphenyl [$^{13}C_{12}$]	PCB167-L	100	(B25)		
3,3′,4,4′,5,5′-Hexachlorobiphenyl [$^{13}C_{12}$]	PCB169-L	100	(B29)		
2,2′,3,4′,5,6,6′-Heptachlorobiphenyl [$^{13}C_{12}$]	PCB188-L	100	(B20)		
2,3,3′,4,4′,5,5′-Heptachlorobiphenyl [$^{13}C_{12}$]	PCB189-L	100	(B30)		
2,2′,3,3′,5,5′,6,6′-Octachlorobiphenyl [$^{13}C_{12}$]	PCB202-L	100	(B26)		
2,3,3′,4,4′,5,5′,6-Octachlorobiphenyl [$^{13}C_{12}$]	PCB205-L	100	(B33)		
2,2′,3,3′,4,4′,5,5′,6-Nonachlorobiphenyl [$^{13}C_{12}$]	PCB206-L	100	(B34)		
2,2′,3,3′,4,5,5′,6,6′-Nonachlorobiphenyl [$^{13}C_{12}$]	PCB208-L	100	(B31)		
Decachlorobiphenyl [$^{13}C_{12}$]	PCB209-L	100	(B35)		
2,4,4′-Trichlorobiphenyl [$^{13}C_{12}$]	PCB28-L	100	B8	15.538	1.372
2,3,3′,5,5′-Pentachlorobiphenyl [$^{13}C_{12}$]	PCB111-L	100	B14	20.872	1.948
2,2′,3,3′,5,5′,6-Heptachlorobiphenyl [$^{13}C_{12}$]	PCB178-L	100	B23	24.672	2.02
2,5-Dichlorobiphenyl [$^{13}C_{12}$]	PCB9-L	100	B4	12.738	0.722
2,2′,5,5′-Tetrachlorobiphenyl [$^{13}C_{12}$]	PCB52-L	100	B9	16.605	1.66
2,2′,4,5,5′-Pentachlorobiphenyl [$^{13}C_{12}$]	PCB101-L	100	B13	19.805	2.165
2,2′,3,4,4′,5′-Hexachlorobiphenyl [$^{13}C_{12}$]	PCB138-L	100	B22	24.472	2.309
2,2′,3,3′,4,4′,5,5′-Octachlorobiphenyl [$^{13}C_{12}$]	PCB194-L	100	B32	30.538	2.237
Cl-PAHs					
9-Chlorofluorene	9-Cl-FLE	4.6	C1	13.606	1.587
9-Chlorophenanthrene	9-Cl-PHE	3.6	C2	17.073	2.67
2-Chloroanthracene	2-Cl-ANT	14	C3	17.339	2.742
9-Chloroanthracene	9-Cl-ANT	6.3	C4	17.339	2.814
3-Chlorofluoranthene	3-Cl-FLA	4.8	C9	23.006	3.319
8-Chlorofluoranthene	8-Cl-FLA	5.4	C10	23.139	3.247
1-Chloropyrene	1-Cl-PYR	5.8	C11	24.273	3.463
6-Chlorochrysene	6-Cl-CHR	5.6	C16	30.073	3.391
7-Chlorobenz[a]anthracene	7-Cl-BaA	10	C17	30.273	3.391

Table 1 (*Continued*)

Compound name	Abbrev	Concentration (ng/ml)	ID[a]	RT on 1st GC (min)	RT on 2nd GC (s)
3-Chlorobenzanthrone	3-Cl-BA-O	23	C18	30.339	3.968
6-Chlorobenzo[a]pyrene	6-Cl-BaP	10	C21	36.339	1.876
3,9-Dichlorophenanthrene	39-Cl2-PHE	7.7	C5	21.073	3.103
1,9-Dichlorophenanthrene	19-Cl2-PHE	3.0	C6	21.339	3.103
9,10-Dichlorophenanthrene	910-Cl2-PHE	2.2	C8	21.673	3.247
9,10-Dichloroanthracene	910-Cl2-ANT	5.1	C7	21.406	3.175
1,3-Dichlorofluoranthene	13-Cl2-FLA	6.3	C13	26.139	2.958
3,8-Dichlorofluoranthene	38-Cl2-FLA	6.9	C14	27.139	3.103
3,4-Dichlorofluoranthene	34-Cl2-FLA	6.7	C15	28.273	3.319
6,12-Dichlorochrysene	612-Cl2-CHR	4.8	C19	32.939	3.319
7,12-Dichlorobenz[a]anthracene	712-Cl2-BaA	5.0	C20	33.139	3.535
3,9,10-Trichlorophenanthrene	3910-Cl2-PHE	5.4	C12	25.139	2.886
PBDEs					
4-Bromodiphenyl ether	BDE3	400	E1	12.206	0.722
2,4-Dibromodiphenyl ether	BDE7	400	E2	15.873	1.876
4,4′-Dibromodiphenyl ether	BDE15	400	E3	17.339	2.165
2,2′,4-Tribromodiphenyl ether	BDE17	400	E4	21.673	2.886
2,4,4′-Tribromodiphenyl ether	BDE28	400	E5	22.539	2.597
2,2′,4,4′-Tetrabromodiphenyl ether	BDE47	400	E8	27.339	2.67
2,2′,4,5′-Tetrabromodiphenyl ether	BDE49	400	E6	26.606	2.67
2,3′,4,4′-Tetrabromodiphenyl ether	BDE66	400	E9	28.139	2.67
2,3′,4′,6-Tetrabromodiphenyl ether	BDE71	400	E7	26.806	2.886
3,3′,4,4′-Tetrabromodiphenyl ether	BDE77	400	E10	29.206	2.67
2,2′,3,4,4′-Pentabromodiphenyl ether	BDE85	400	E14	33.206	3.103
2,2′,4,4′,5-Pentabromodiphenyl ether	BDE99	400	E13	31.606	2.742
2,2′,4,4′,6-Pentabromodiphenyl ether	BDE100	400	E11	30.606	2.742
2,3′,4,4′,6-Pentabromodiphenyl ether	BDE119	400	E12	31.006	2.814
3,3′,4,4′,5-Pentabromodiphenyl ether	BDE126	400	E15	33.606	2.886
2,2′,3,4,4′,5-Hexabromodiphenyl ether	BDE138	800	E18	37.139	1.659
2,2′,4,4′,5,5′-Hexabromodiphenyl ether	BDE153	800	E17	35.273	3.896
2,2′,4,4′,5,6′-Hexabromodiphenyl ether	BDE154	800	E16	33.939	3.103
2,3,3′,4,4′,5-Hexabromodiphenyl ether	BDE156	800	E19	38.006	2.381
2,2′,3,4,4′,5′,6-Heptabromodiphenyl ether	BDE183	800	E21	39.406	3.896
2,2′,3,4,4′,6,6′-Heptabromodiphenyl ether	BDE184	800	E20	38.539	3.175
2,3,3′,4,4′,5′,6-Heptabromodiphenyl ether	BDE191	800	E22	40.939	1.587
2,2′,3,3′,4,4′,5,6′-Octabromodiphenyl ether	BDE196	800			
2,2′,3,3′,4,4′,6,6′-Octabromodiphenyl ether	BDE197	800			
2,2′,3,3′,4,4′,5,5′,6-Nonabromodiphenyl ether	BDE206	2000			
2,2′,3,3′,4,4′,5,6,6′-Nonabromodiphenyl ether	BDE207	2000			
Decabromodiphenyl ether	BDE209	2000			
4-Bromodiphenyl ether [$^{13}C_{12}$]	BDE3-L	100	(E3)		
4,4′-Dibromodiphenyl ether [$^{13}C_{12}$]	BDE15-L	100	(E3)		
2,4,4′-Tribromodiphenyl ether [$^{13}C_{12}$]	BDE28-L	100	(E5)		
2,2′,4,4′-Tetrabromodiphenyl ether [$^{13}C_{12}$]	BDE47-L	100	(E8)		
2,2′,4,4′,5-Pentabromodiphenyl ether [$^{13}C_{12}$]	BDE99-L	100	(E13)		
2,2′,4,4′,5,5′-Hexabromodiphenyl ether [$^{13}C_{12}$]	BDE153-L	200	(E17)		
2,2′,4,4′,5,6′-Hexabromodiphenyl ether [$^{13}C_{12}$]	BDE154-L	200	(E16)		
2,2′,3,4,4′,5′,6-Heptabromodiphenyl ether [$^{13}C_{12}$]	BDE183-L	200	(E21)		
2,2′,3,3′,4,4′,6,6′-Octabromodiphenyl ether [$^{13}C_{12}$]	BDE197-L	200			
2,2′,3,3′,4,4′,5,6,6′-Nonabromodiphenyl ether [$^{13}C_{12}$]	BDE207-L	500			
Decabromodiphenyl ether [$^{13}C_{12}$]	BDE209-L	500			
2,2′,3,4,4′,5′-Hexabromodiphenyl ether [$^{13}C_{12}$]	BDE138-L	200	(E18)		
Br-PAHs					
2-Bromofluorene	2-Br-FLE	11	R1	15.539	1.948
9-Bromophenanthrene	9-Br-PHE	13	R2	19.406	30175
9-Bromoanthracene	9-Br-ANT	9.7	R3	19.806	3.247
9,10-Dibromoanthracene	910-Br2-ANT	10	R4	26.139	30175
1-Bromopyrene	1-Br-PYR	11	R5	26.606	3.319
7-Bromobenz[a]anthracene	7-Br-BaA	10	R6	32.206	3.39
7,11-Dibromobenz[a]anthracene	711-Br2-BaA	10			
7,12-Dibromobenz[a]anthracene	712-Br2-BaA	10			
4,7-Dibromobenz[a]anthracene	47-Br2-BaA	9.5			
5,7-Dibromobenz[a]anthracene	57-Br2-BaA	9.5			
6-Bromobenzo[a]pyrene	6-Br-BaP	11			

[a] These IDs are shown in Figs. 1 and 2.

of air [21,22] were detected by coupling the GC × GC-HRTofMS and a thermal desorption unit (TDU). However, we also confirmed certain disadvantages with the GC × GC-HRTofMS, namely that the dynamic range of the detector was insufficient for environmental pollutants distributed at various concentrations and the amount of data was too great to deal with easily.

Therefore, we are developing a new system consisting of a GC × GC directly coupled with a quadrupole type tandem mass spectrometer (MS/MS) to overcome the disadvantages of GC × GC-HRTofMS. The GC × GC–MS/MS is not yet widely used although Poliak et al. have reported the development of a flow modulating GC × GC interfaced with an MS/MS by using supersonic molecular beam ionization for multiple reaction monitoring (MRM) [23]. We are using the GC × GC–MS/MS to develop new methods for the simultaneous quantification of many compounds including dioxins, PCBs and other POPs. We are also studying the global and selec-

tive detection of organic pollutants in environmental and biological samples by using the high resolving power of the GC × GC and the selective detection of specific compounds by using the neutral loss scan (NLS) mode of the MS/MS.

In this paper, we report our first attempt to detect halogenated compounds comprehensively and selectively in environmental samples by employing the NLS mode of the GC × GC–MS/MS, and we identify some of these compounds with the GC × GC-HRTofMS. Additionally, we have developed software that creates simulated NLS data from the mass spectra of the GC × GC-HRTofMS to assist in finding halogenated compounds in the data obtained from those instruments.

2. Experimental

2.1. Samples and sample preparation

Fly ash extract (certified reference material; NIES CRM No. 17, toluene solution), sediment (National Institute for Environmental Studies (NIES) CRM No. 20), soil (NIES CRM No. 21) and flue gas extract (from municipal waste incinerators in Japan, toluene solution) [20] were provided for this study. Sediment and soil samples were extracted using a Soxhlet extractor with toluene over a period of 24 h, and then the extracts were concentrated and resolved into hexane. The hexane solution was cleaned in a chromatography column containing 5 g of sulfuric acid silica gel (44% sulfuric acid/silica gel (w/w) for dioxin analysis, Wako Pure Chemical Industries, Osaka, Japan), and the hexane solution (100 ml) eluted from the column was concentrated and dissolved into 100 μl of toluene for measurement.

2.2. Chemicals

^{13}C labeled and non-labeled PCDD/F standard mixture solution (35 compounds, EPA-1613-CS calibration standards, Wellington Laboratories, Canada), ^{13}C labeled and non-labeled PCBs standard mixture solution (62 compounds, 68B-CS calibration standards, Wellington Laboratories), ^{13}C labeled and non-labeled POP standard mixture solution (43 compounds, ES-5348 calibration standards, Cambridge Isotope Laboratories Inc. (CIL), MA, USA), ^{13}C labeled and non-labeled PBDE standard mixture solution (39 compounds, BDE-CS calibration standards, Wellington Laboratories), 21 chlorinated and 11 brominated PAHs synthesized by Ohura et al. [24], which are listed in Table 1, were used for checking the retention times in bidimensional chromatograms and for identifying halogenated compounds.

2.3. Measurement instruments and conditions

Samples were measured using a 7890GC (Agilent Technologies, Palo Alto, CA, USA) with a KT2006 GC × GC system (Zoex, Houston, TX, USA) coupled with a 7000A (Agilent Technologies) MS/MS and a 6890GC (Agilent Technologies) with a KT2004 GC × GC system (Zoex) coupled with a JMS-T100GC (JEOL, Tokyo, Japan) HRTofMS. A column pair consisting of 5% phenyl/phenyl–methyl silicone and 50% phenyl/phenyl–methyl silicone was employed as the liquid phase of the GC capillary columns for measurements with the GC × GC systems. The first GC capillary column was an InertCap 5MS/Sil (60 m length, 0.25 mm i.d., 0.1 μm film thickness, GL Sciences, Tokyo, Japan) and the second was a BPX-50 (1.5 m length, 0.1 mm i.d., 0.1 μm film thickness, SGE Analytical Science, Victoria, Australia). The conditions and parameters of the GC × GC–MS/MS and the GC × GC-HRTofMS used for the PCDDs/Fs measurements are shown in Table 2.

Table 2
GC × GC–MS/MS and HRTofMS conditions for organohalogens.

GC × GC	
Instrument	Agilent 7890 GC (for Agilent 7000A) or Agilent 6890 GC (for JMS-T100GC)
GC × GC	Zoex KT2006 (in 7890 GC) or KT2004 ()
1st column	GL Science InertCap 5MS/SN (60 m length, 0.25 mm i.d., 0.1 μm film thickness)
2nd column	SGE BPX-50 (1.5 m length, 0.1 mm i.d., 0.1 μm film thickness)
Oven program	from 70 °C holding for 1 min to 180 °C at rate 50 °C min^{-1} holding for 0 min to 230 °C at rate 3 °C min^{-1} holding for 0 min to 300 °C at rate 5 °C min^{-1} holding for 16.133 min
Injection	volume: 1 μl, temp: 280 °C, method: splitless
Carrier gas	type: He, mode: constant flow, initial head pressure: 488.8 kPa at 70 °C
Modulation	period: 4 s, releasing: 0.35 s
MS/MS	
Instrument	Agilent 7000A (7000B equivalent)
Ion source	mode: EI+, temp: 250 °C, ionizing voltage: 40 V, ionizing current: 35 μA
Analyzer	mode: neutral loss scan, monitoring loss[a]: 19, 35, 37, 79, 81 *m*/*z* scan range: 150–530 *m*/*z*, cycle: 20 Hz
HRTofMS	
Instrument	JEOLJMS-T100GC
Ion source	mode: EI+, temp: 250 °C, ionizing voltage: 35 V, ionizing current: 600 μA
Analyzer	resolution: 5000, recording range: 35–550 *m*/*z*, cycle: 25 μHz
Detector	MCP voltage: 2700 μV

[a] The monitored neutral loss was a single setting and was not changed during a measurement.

2.4. Data processing

Data obtained from the Agilent 7000A were converted to the *mz*-data format on a MassHunter rev.b.4.2 (Agilent Technologies). Mass profile data acquired with the JEOL JMS-T100GC were converted into mass spectra, and then transformed into text data (.csv) in several steps. First, AIA-formatted data were converted from raw data using a data exportation function in the software bundled with the JEOL JMS-T100GC. Then the text data were converted from the AIA-formatted data by the command "Convert Chromatogram Files" in Palisade MASSTransit v.2.6.2 (Newfield, NY, USA). The converted data were loaded onto a GC Image v.2.1.2 custom edition for NIES (GC Image LLC, NE, USA), and two- or three-dimensional chromatograms were drawn. The GC Image was equipped with a "GC × GC × MS 3D Viewer", which can display mass spectra on the *z*-axis as well as 2D-chromatograms on the *x*–*y* axis. We used the function for visual confirmation of the distinctive isotope pattern of chlorine or bromine in each peak.

2.5. Creating artificial neutral loss scan data from mass spectra of HRTofMS

After the data from the JEOL JMS-T100GC were converted to a text file through the above process, artificial neutral loss scan data were created from the text file using novel software. The simulated data were reconverted to AIA-formatted data by MASSTransit, and then analyzed on GC Image.

The novel software was built by Microsoft Visual Studio 2008# (Redmond, WA, USA) and operates on Microsoft Windows (both 32-bit and 64-bit versions). The program searches from lower to higher mass in each mass spectrum, and then extracts only the mass (m) and the abundance from the spectrum when it finds an abundance at a mass ($m+x$); where x is the mass of the neutral loss given by a user, for example 34.969 as ^{35}Cl, 78.918 as ^{79}Br, etc. This program

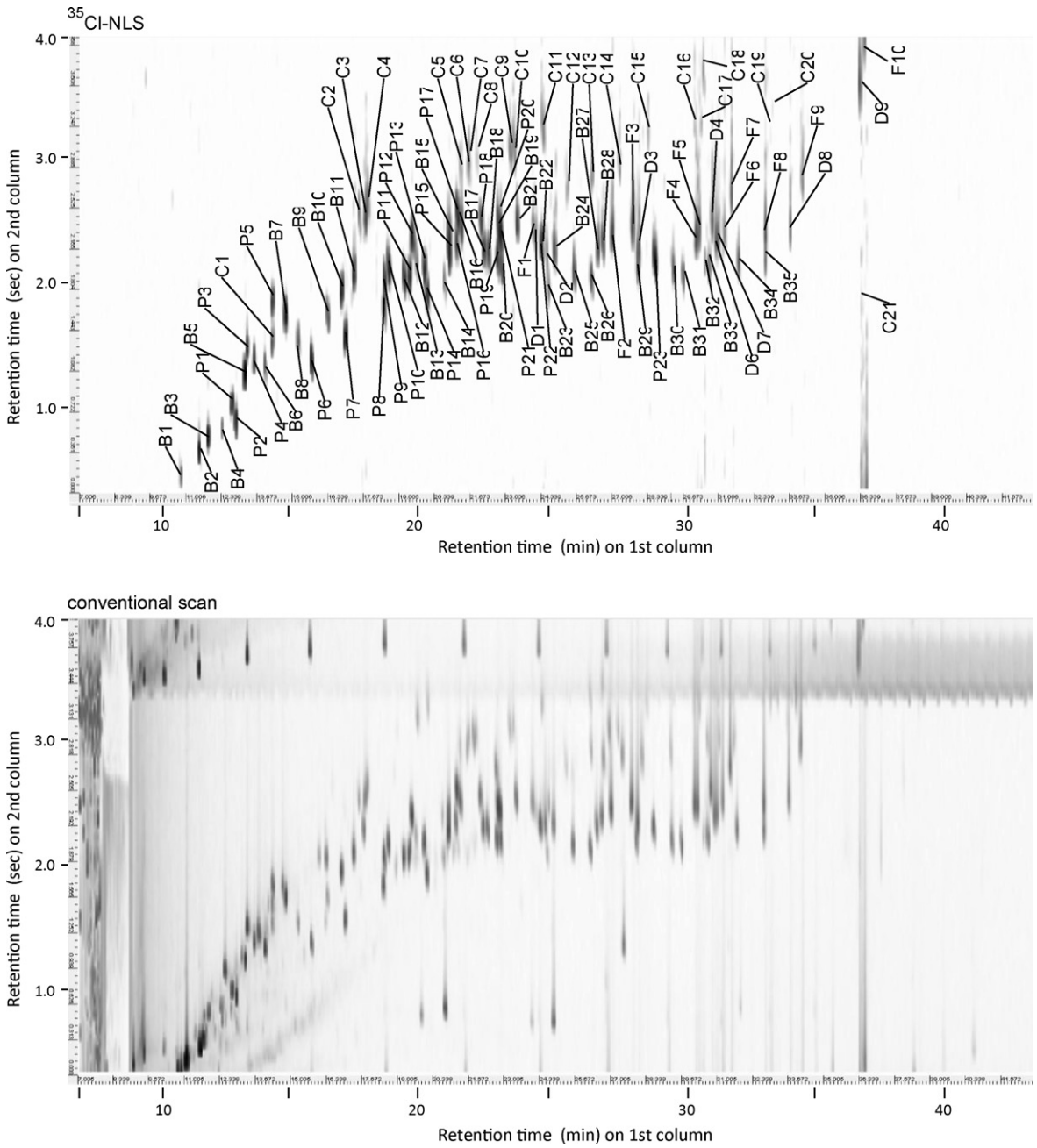

Fig. 1. Two-dimensional total ion chromatograms (TICs) of standard organohalogens (Measured organohalogens are listed in Table 1. The letters and numbers in the ^{35}Cl-NLS 2D-TIC can also be found in the table.) measured with a ^{35}Cl-neutral loss scan (NLS, upper) and a conventional scan (lower) with the GC × GC–MS/MS.

can also create artificial neutral gain data. In such a case, it extracts only the mass (m) and the abundance from the spectrum when it finds an abundance at a mass ($m - x$).

3. Results and discussion

3.1. Measurement of standards in neutral loss scan mode by GC × GC–MS/MS

The standards of the 211 organohalogen compounds (16 PCDDs, 19 PCDFs, 62 PCBs, 39 PBDEs, 21 chlorinated PAHs, 11 brominated PAHs and 43 the other POPs) listed in Table 1 were measured in a neutral loss scan (NLS) mode with the GC × GC–MS/MS to optimize the conditions and parameters of the instrument and thus achieve high levels of separation and sensitivity analysis. In Fig. 1, the result when a neutral loss of 34.97 (m/z) was monitored while assuming the defragmentation of ^{35}Cl is displayed as a two-dimensional total ion chromatogram (2D-TIC) with a 2D-TIC of a conventional mass scan (m/z = 150–530). All of the chlorinated standard compounds were detected and no interference peak or band was observed in the 2D-TIC of a ^{35}Cl-NLS whereas many peaks probably including other compounds appeared in the chromatogram of a conventional scan. Similarly, brominated standard compounds were selectively detected by an NLS, which monitored a neutral loss of 78.92 (m/z) assuming the defragmentation of ^{79}Br (Fig. 2). These results show that an NLS was effective in selectively detecting halogenated compounds.

Mixed halogen compounds containing several species of halogen, *i.e.* Cl and Br, F and Cl, could be identified by overlapping NLS 2D-chromatograms for each halogen loss. In fact, the retention time

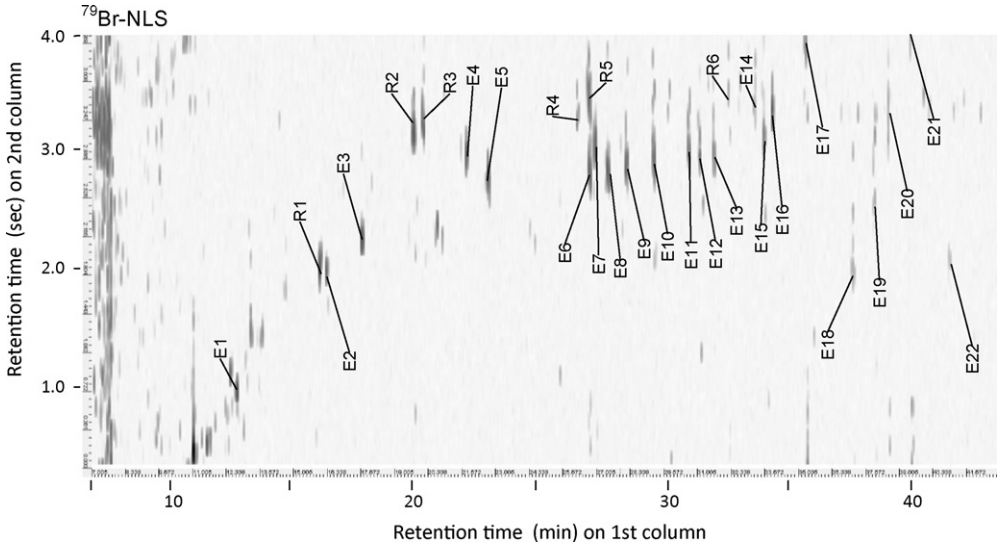

Fig. 2. Two-dimensional total ion chromatograms (TICs) of standard organohalogens (Measured organohalogens are listed in Table 1. The letters and numbers in the 2D-TIC can also be found in the table.) measured with a ^{79}Br-neutral loss scan with the GC × GC–MS/MS.

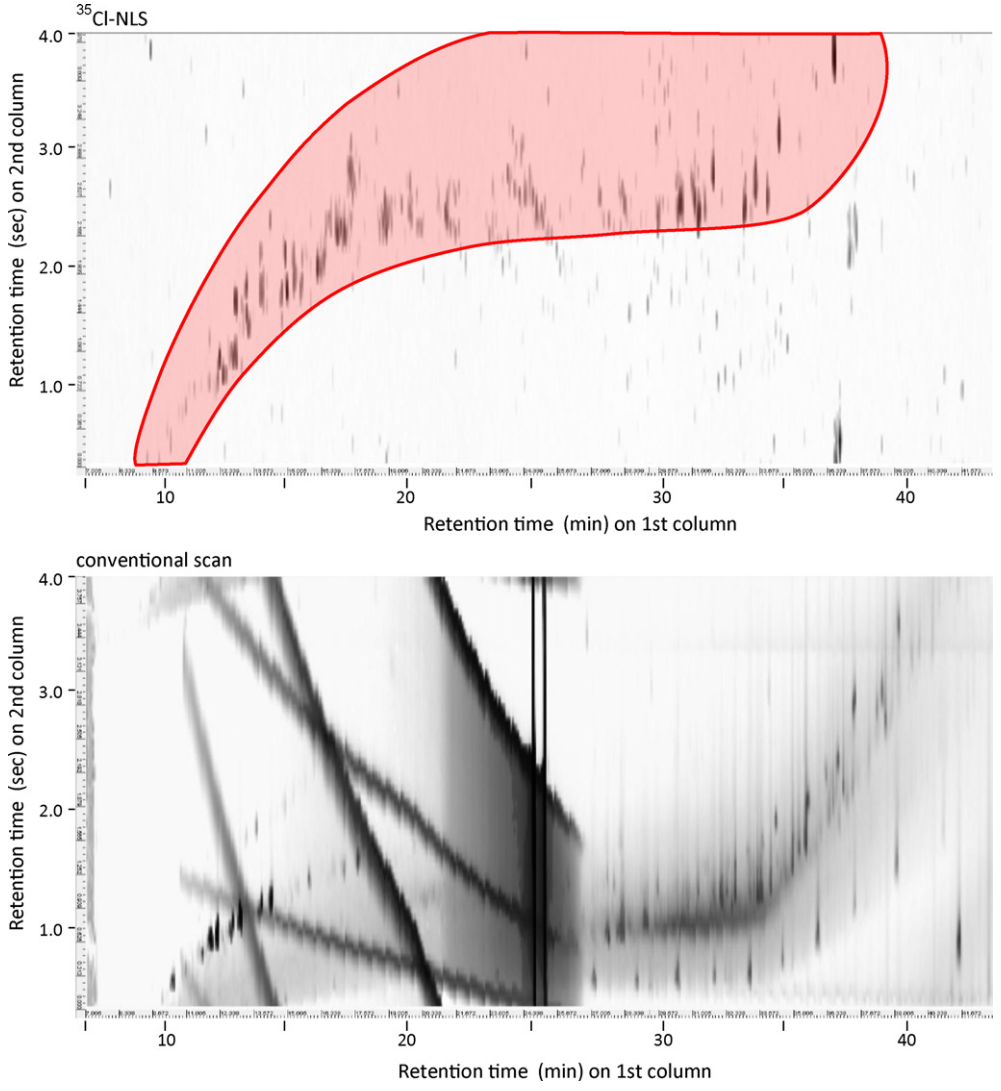

Fig. 3. Two-dimensional total ion chromatograms (TICs) of a sediment sample (NIES CRM20) measured with a ^{35}Cl-neutral loss scan (NLS, upper) and a conventional scan (lower) with the GC × GC–MS/MS. The red translucent shape in the upper chromatogram shows the area where organohalogens are expected to appear. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

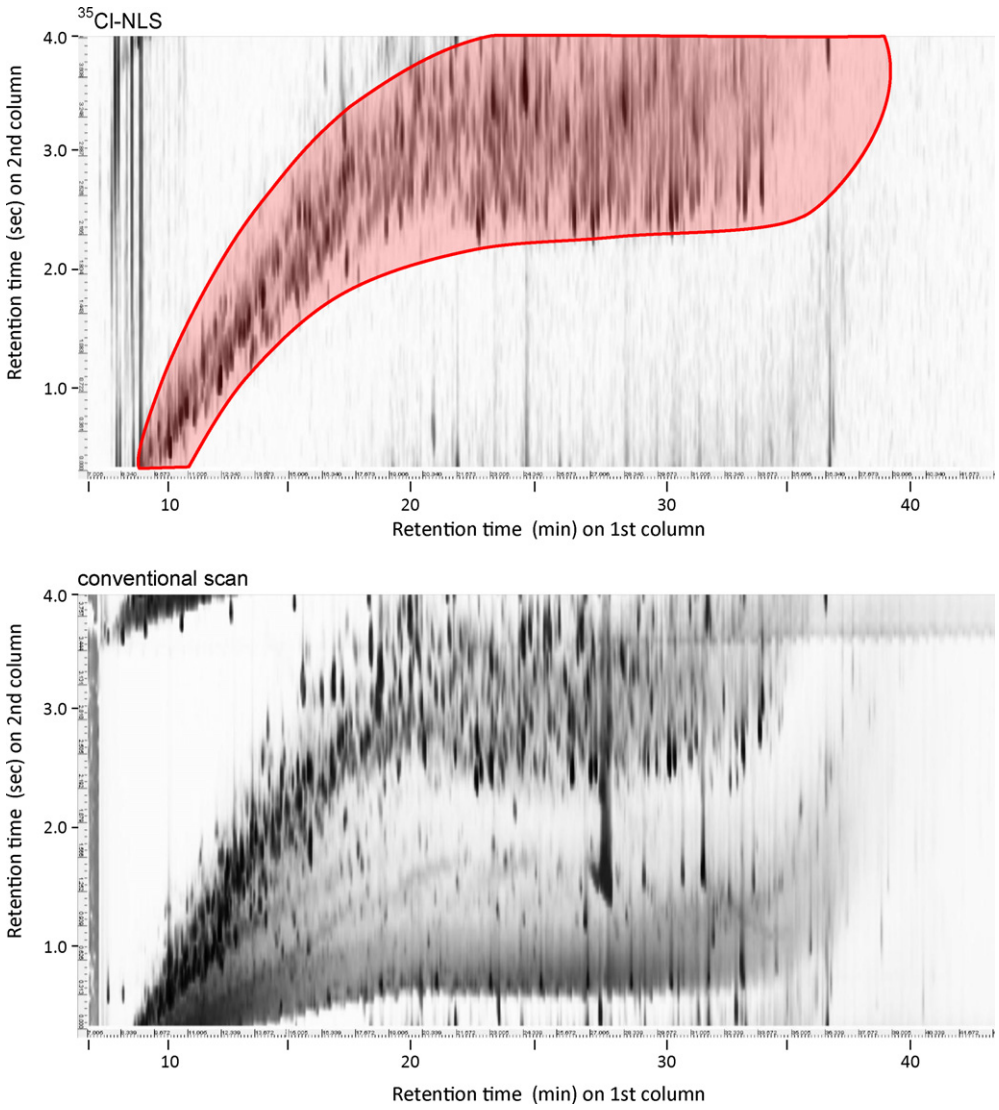

Fig. 4. Two-dimensional TICs of fly ash extract (NIES CRM17) measured with a ^{35}Cl-NLS (upper) and a conventional scan (lower) obtained with the GC × GC–MS/MS. The red translucent shape in the upper chromatogram shows the area where organohalogens are expected to appear. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

of Cl/Br–pyrene coincided in each 2D-chromatogram of ^{35}Cl- and ^{79}Br-NLS.

3.2. Measurement of environmental samples in NLS by GC × GC–MS/MS

Environmental samples such as fly ash extract, and soil and sediment pretreated extracts were measured in the NLS mode by the GC × GC–MS/MS under the same conditions, which were obtained from standard measurements. The results of a ^{35}Cl-NLS and a conventional scan (m/z = 150–530) of the sediment sample are shown as 2D-TICs in Fig. 3. Although a huge number of peaks and bands of complex compounds were observed in the chromatogram obtained with a conventional scan, many peaks were isolated by a ^{35}Cl-NLS of the sediment sample. Similarly, many peaks assumed to be organochlorines were selectively detected in the 2D-TIC of a ^{35}Cl-NLS for the fly ash extract whereas a large number of peaks appeared throughout the chromatogram obtained with a conventional scan as shown in Fig. 4. The peaks in the 2D-TIC of a ^{35}Cl-NLS were distributed between peaks estimated as non-substituted alkanes and PAHs in the 2D-TIC of a conventional scan and this was consistent with previous reports [25,26]. It is interesting that a large number of peaks (approximately 1000) were detected from the fly ash extract by a ^{35}Cl-NLS. This probably suggests the existence of organohalogens other than dioxins and PCBs. Flue gas and soil samples were also measured using a ^{35}Cl-NLS and a conventional scan. Some peaks of chlorinated compounds were isolated from the samples. However, the number of peaks was obviously smaller than for the fly ash extract. In this study, the detection limit of a ^{35}Cl-NLS was roughly estimated based on three times the signal to noise (S/N) ratio of each standard compound on the 2D-TIC being around 100–1000 pg for organohalogen compounds such as PCBs and dioxins. There was still a lack of sensitivity as regards environmental samples while sharp peaks from the GC × GC contributed to improving the S/N ratio compared with a single GC. Additionally, it was also suspected that a significant loss of organohalogens occurred via the sulfuric acid column chromatography. Here, we employed a coarse cleanup approach to reduce the damage to the GC separation induced by oily or polar matter in the sample because we knew from our experience and that of other researchers that the sediments contained complex organic matter [25]. In terms of global detection, the result was a compromise.

For the fly ash extract and sediment pretreated extract, the distribution region of the peaks collected at the 2D-TIC of the ^{35}Cl-NLS

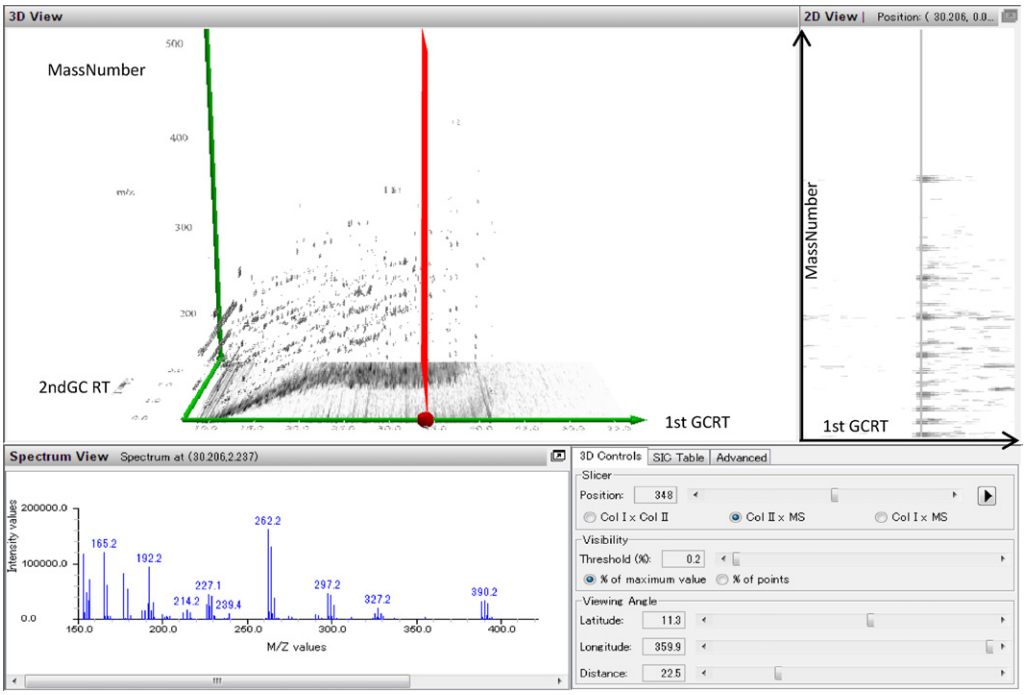

Fig. 5. Screen shot of "GC × GC × MS 3D Viewer" on GCImage, displaying the fly ash extract (NIES CRM17) data measured with an NLS monitored 35 m/z loss on the GC × GC–MS/MS. The top left pane "3D View" shows a 3D matrix where the x, y and z axes indicate the retention time on the 1st and 2nd GC, and mass, respectively. The top right pane "2D View" shows a sectional view indicated by a thin rectangle on the 3D matrix. The bottom left pane "Spectrum View" shows a mass spectrum indicated with a gray line in the sectional view.

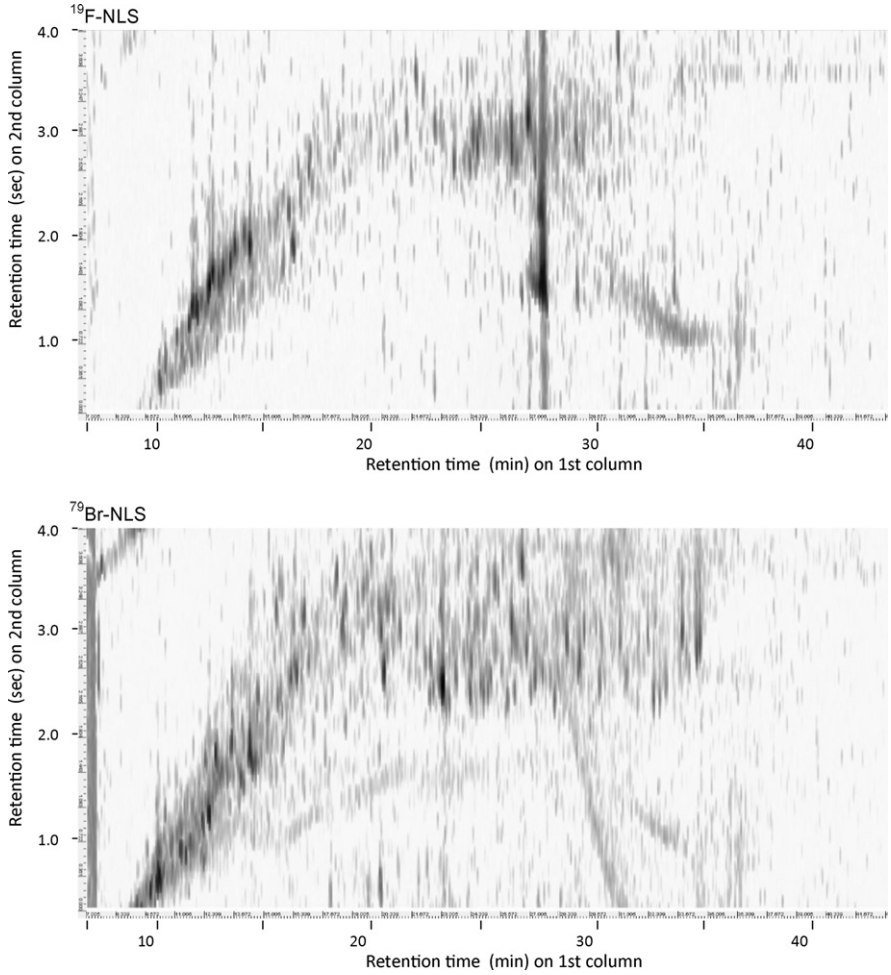

Fig. 6. Two-dimensional TICs of fly ash extract (NIES CRM17) measured with a ^{19}F-NLS (upper) and a ^{79}Br-NLS (lower) with the GC × GC–MS/MS.

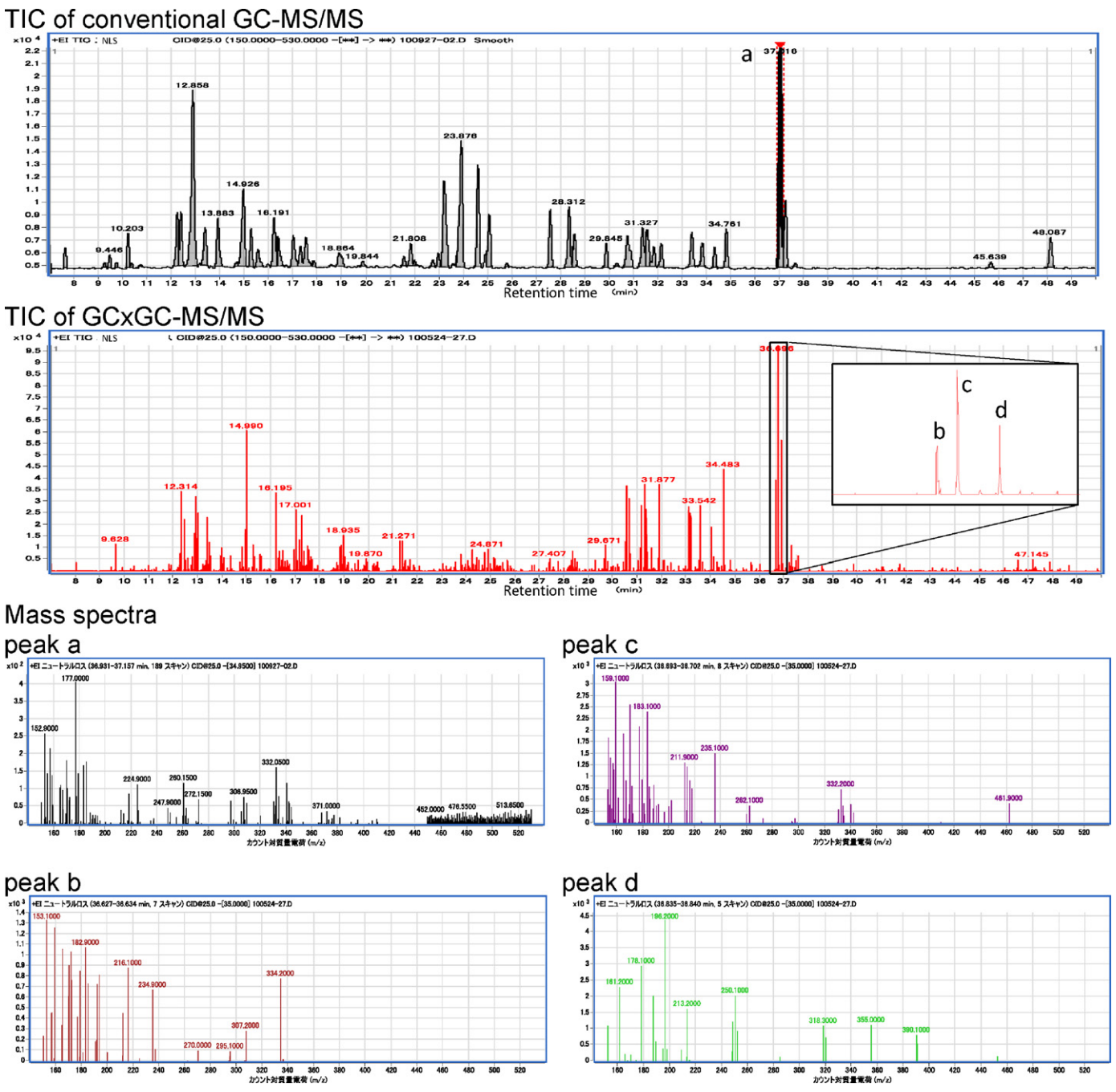

Fig. 7. TIC and mass spectra of a sediment sample (NIES CRM20) measured with a ^{35}Cl-NLS obtained with a conventional GC–MS/MS and a GC × GC–MS/MS. Upper and lower TICs obtained with a conventional GC–MS/MS and the GC × GC–MS/MS, respectively. The other four images show the mass spectra of peaks a, b, c and d, respectively.

overlapped with the retention times of the PCBs, PCDDs and PCDFs as shown in Figs. 1 and 3 or 1 and 4. Additionally, many PCB, PCDD and PCDF congeners were found in the peaks at the same retention times in the 2D-chromatograms of conventional scans as those of a ^{35}Cl-NLS obtained by a library search using the Wiley Registry 8th edition/NIST 2005 Mass Spectral Library (John Wiley & Sons, Inc., NJ, USA). The "GC × GC × MS 3D Viewer", which was one of the tools in GC Image customized for our research, was very useful for finding halogenated compounds in a 2D-chromatogram obtained with a conventional scan, because it can display mass spectra on the z-axis for an entire 2D-chromatogram as shown in Fig. 5. In this example, many clustered ions of chlorine isotopes could be observed along the z-axis in the top left pane "2D View" of the window in Fig. 5.

In the same way, many peaks were detected by employing a ^{79}Br-NLS and a ^{19}F-NLS for the environmental samples. Fig. 6 shows the 2D-TIC of a ^{79}Br-NLS and a ^{19}F-NLS of the fly ash extract, and expected brominated or fluorinated compounds appeared in each chromatogram. Some of the peaks in the chromatograms of the ^{19}F-NLS, ^{35}Cl-NLS and ^{79}Br-NLS were located at the same retention times, and this suggests that the environment contains a mixed halogenated compound that includes several species of halogen atom. However, we could not identify the mass spectra of those peaks because our instrument was insufficiently sensitive and there was a library search mismatch.

As described above, the GC × GC–MS/MS delivered superior performance as regard the separation and selective detection of organohalogens, especially of organochlorines. Fig. 7 shows chro-

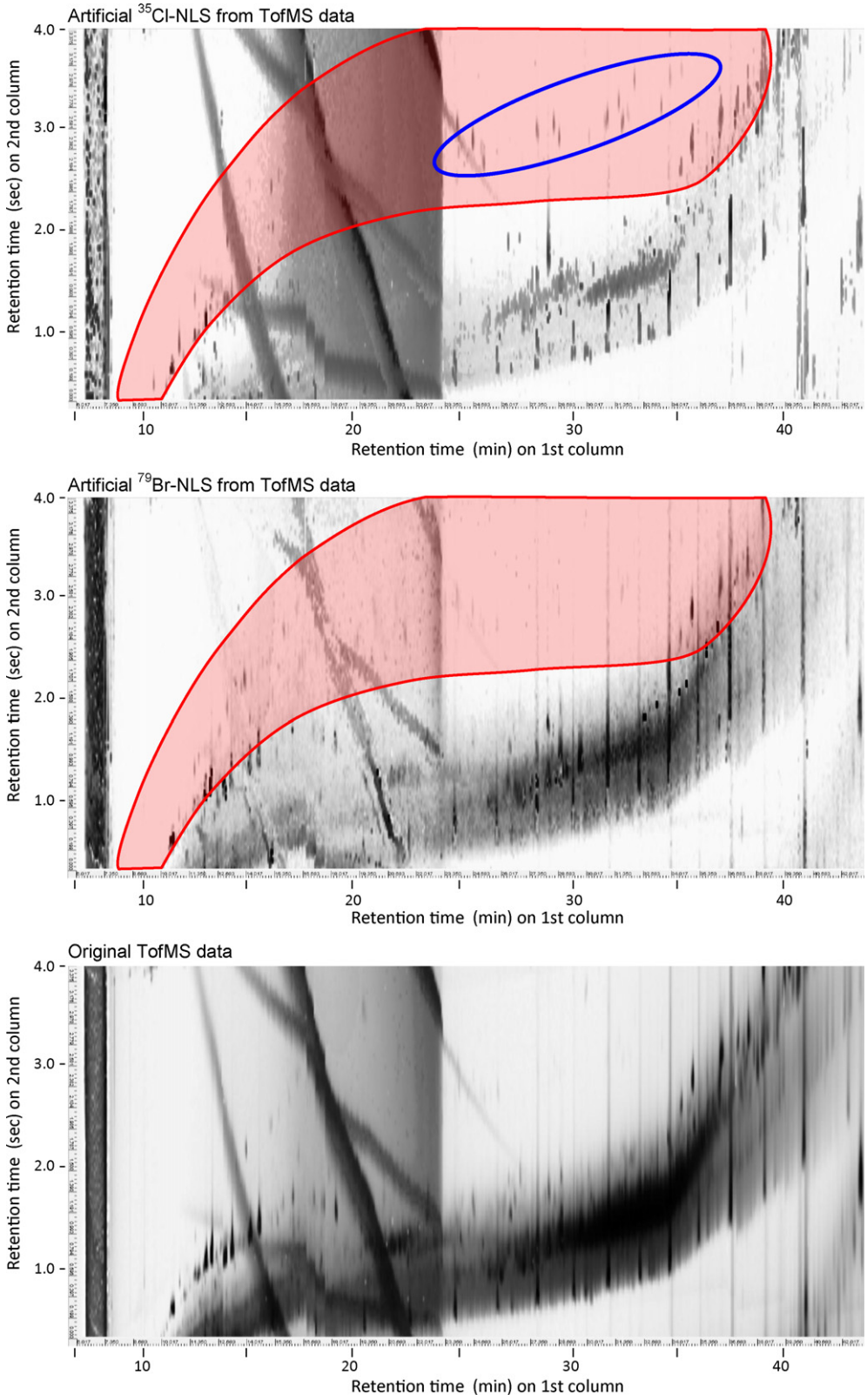

Fig. 8. Two-dimensional TICs of sediment (NIES CRM20) extract washed with sulfuric acid; artificial neutral loss scan for 35 (top) and 79 (middle) in 50–550 (*m*/*z*) recomposed from HRTofMS data with original software, and the original data (bottom) from the GC × GC-HRTofMS. Several peaks are observed in a blue ellipse only in the 2D-TIC of artificial ^{35}Cl-NLS from TofMS data. Red translucent shapes in the chromatograms show areas where organohalogens are expected to appear. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

matograms of a ^{35}Cl-NLS obtained with a conventional GC–MS/MS (upper chromatogram) and with a GC × GC–MS/MS (lower chromatogram) for the sediment extract. There appear to be fewer peaks in the upper chromatogram than the lower one or the 2D-chromatogram shown in Fig. 3 (upper picture). For example, the peak at 37.016 min in the chromatogram obtained by the GC–MS/MS was separated into three major peaks by the GC × GC–MS/MS and these mass spectra support the isolation of the peak components. It shows that the separating power of a conventional GC is insufficient to isolate each peak from a complex matrix in a crude sample even when an MS/MS is used as a detector. Therefore, the coupling of a GC × GC and an MS/MS can be an effective approach for the complete global detection of organohalogens.

3.3. Searching for and identifying compounds with GC × GC-HRTofMS

The samples were also measured with the GC × GC-HRTofMS under the same conditions as those used with the GC × GC–MS/MS. A mass spectrum in the 2D-chromatogram obtained with the GC × GC-HRTofMS at the same retention time as one obtained with the GC × GC–MS/MS was searched for in the mass spectral library and its nominal composition was investigated from its accurate mass profile. In this way, several congeners of polychlorinated dibenzo-*p*-dioxin and their halogenated compounds such as PCBs and chlorinated PAHs were found in the 2D-chromatograms obtained from the GC × GC-HRTofMS. However, most of peaks, which were suggested inclusion of chlorine or bromine atom(s) by the mass spectra, were not matched in the mass library searching.

In this study, we attempted to recompose artificial NLS data from HRTofMS data to extract specific information from a large amount of GC × GC-HRTofMS data. Fig. 8 shows 2D-TICs of an artificial ^{35}Cl-NLS (top) and a ^{79}Br-NLS (middle) recomposed from the GC × GC-HRTofMS data of a sediment sample with our own software (see Section 2.5). The peaks and bands in those TICs were smaller than in the original TIC (bottom in Fig. 8) although it is difficult to say that the software completely replicated the neutral loss scan of the GC × GC–MS/MS. The peaks in the area where dioxins and PCBs should appear were more clearly isolated than those in the 2D-TIC of the unprocessed data. This shows that the approach has the potential to elicit useful information from the complicated data of the GC × GC-HRTofMS although the software algorithms may need improving to enhance the feasibility of using this method in the future. For example, we should consider the value of combining it with methods that extract compounds from the GC × GC-TofMS data based on information such as retention time and major mass fragments and proposed by Welthagen et al. [27] and Vogt et al. [28].

4. Conclusion

The direct measurement of samples without any compound loss is ideal for the complete global detection of pollutants.

The results of this study show that a neutral loss scan with MS/MS was effective in selectively detecting halogenated compounds, especially those with more than two halogen substituents, in environmental samples. However, a conventional gas chromatograph cannot separate the huge number of compounds contained in a crude sample even when an MS/MS is used as a detector. Therefore, the coupling of a GC × GC and an MS/MS is an effective approach for the complete global detection of organohalogens.

In the future, we can expect to achieve the complete global detection of any compound in one measurement of a crude sample simply with a GC × GC-HRTofMS if it becomes possible to extract the desired information from the GC × GC-HRTofMS data.

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