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Monitoring of herbicides in river water by gas chromatography–mass spectrometry and solid-phase extraction

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Abstract

A gas chromatography–mass spectrometric method was developed to determine concentrations of herbicides in both the dissolved phases and the suspended phase of river water. The target herbicides were 2-amino-3-chloro-1,4-naphthoquinone, alachlor, benfluralin, bifenox, bromobutide, the debromo form of bromobutide, butachlor, butamifos, chlomethoxyfen, chlornitrofen, chlorpropham, dimepiperate, dimethametryn, dithiopyr, esprocarb, MCPA-ethyl, MCPA-thioethyl, mefenacet, molinate, naproanilide, oxadiazon, pendimethalin, piperophos, pretilachlor, prometryn, simazine, simetryn, thiobencarb and trifluralin. The herbicides in filtered river water were extracted with styrene–divinylbenzene copolymer and were eluted with acetone. The herbicides on suspended substances were extracted ultrasonically with acetone. Recoveries of the herbicides on the overall performance of this method were 81.6% to 128% from filtered river water and 80.0% to 110% from suspended substances. The minimum detectable concentrations in water and suspended substances ranged from 0.01 $\mu g\ l^{-1}$ to 0.02 $\mu g\ l^{-1}$ and 0.05 $\mu g\ g^{-1}$ to 0.1 $\mu g\ g^{-1}$, respectively. This method was successfully applied to monitoring herbicides in river water.

Keywords: Environmental analysis; Water analysis; Sample preparation; Pesticides

1. Introduction

Many kinds of herbicides are used for agricultural processes as well as for non-agricultural purposes. Their variations in environmental water have been monitored in several districts [1–5]. There have been a number of reports describing developments in methods to analyze herbicides in environmental water samples [1,3,4,6–10]. Recently, a solid-phase pre-extraction method has been a common method for gas chromatographic (GC) or gas chromatography–mass spectrometric (GC–MS) determination. Octadecyl (C_{18}) bound to porous silica has been the most used device for solid-phase extraction [1,6–13]. Junk and Richard [6] used C_{18}-bound silica for GC analysis of seven herbicides spiked to surface water; Scott [10] reported a GC determination of four herbicides in portable water by C_{18}-bound silica extraction. Huang [7] reported a GC–MS method for another four herbicides. Lately, styrene–divinylbenzene copolymer has been recommended as an extractor for some regulated pesticides by the Japanese Ministry of Health and Welfare [14] and the Environmental Agency of Japan [15]. Although many herbicides are applied, few works have described the simultaneous determination of herbicides.

Almost all previous reports deal with the target compounds that exist only in filtered environmental water [6,10,16], because most parts of pesticides may be soluble in water. Pereila and Rosted [1] reported that 99.5% of five herbicides, simazine, atrazine, alachlor, metolachlor and cyanazine, were

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in the dissolved phase in the Mississippi River, USA. On the other hand, Hinckley and Bidleman [17] reported that 77% of the insecticide, fenvalerate, was found on particulate matter in water from Leadenwah Creek, SC, USA. However, only few works have described methods for the determination of herbicides in river water distributed into the water phase and the solid phase. Hence, there have been few reports on partitioning of other herbicides in environmental water.

Therefore, we developed a GC–MS method for the simultaneous determination of 29 herbicides in the two phases, and applied the method to monitor herbicides in river water. Styrene–divinylbenzene copolymer was selected as the solid phase for extraction of herbicides from filtered water. The herbicides investigated were 2-amino-3-chloro-1,4-naphthoquinone (ACN), alachlor, benfluralin, bifenox, (*RS*)-1-bromo-N-(α,α-dimethylbenzyl)-2,2-dimethylpropamide (bromobutide), the debromo form of bromobutide (bromobutide-debromo), butachlor, butamifos, chlomethoxyfen, chlornitrofen, chlorpropham, dimepiperate, dimethametryn, dithiopyr, esprocarb, the ethyl ester of 2-methyl-4-chlorophenoxyethanoic acid (MCPA-ethyl), MCPA-thioethyl, mefenacet, molinate, naproanilide, oxadiazon, pendimethalin, piperophos, pretilachlor, prometryn, simazine, simetryn, thiobencarb and trifluralin. These herbicides are commonly used in Japan for agricultural and non-agricultural purposes.

2. Materials and methods

2.1. Apparatus and materials

A Waters Sep-Pak Concentrator (Nihon Millipore, Tokyo, Japan) and a SPE Manifold (J & W, Folsom, CA, USA) were used for solid-phase extraction and elution, respectively. A mass spectrometer Automass 50 (JEOL, Tokyo, Japan) equipped with a gas chromatograph, HP-5890 II (Hewlett-Packard, Avondale, PA, USA), was used for quantitative analysis. Herbicides were purchased from Wako (Osaka, Japan), Kanto (Tokyo, Japan) and GL Science (Tokyo, Japan). Other reagents were purchased from Wako. All solvents used were of pesticide-grade. A solution containing a mixture of *n*-alkanes with carbon numbers 11–30 (except for 29), that was used to measure the temperature-programmed retention index (I) of each herbicide and of the internal standard was purchased from Hewlett-Packard. A PEG solution was prepared using acetone with PEG 200 and PEG 300 (10 000 μg ml^{-1}) to make herbicide peaks sharp and symmetrical ([18]). An acetone solution containing 200 μg ml^{-1} of 1,4-diiodobenzene and 9-bromoanthracene was prepared as an internal standard solution. All standard solutions of herbicides for GC–MS determination were prepared by addition of 10 μl of the PEG solution and 5 μl of the internal standard solution per milliliter of them. The Waters Sep-Pak Plus PS-2 cartridges (Nihon Millipore) were washed with 5 ml of acetone, followed by 5 ml of distilled water prior to use. A 1-μm pore size glass-fiber filter, GA-100 (Toyo Roshi, Tokyo, Japan), of 47 mm diameter was heated at 450°C for 4 h before use.

2.2. Determination procedure

Water samples were filtered through the glass-fiber filter contained in a glass filter holder. A 500-ml volume of filtered water was passed through the cartridges at a flow-rate of 10 ml min^{-1}. After the cartridges were washed with 10 ml of distilled water, they were dried by drawing in air from the room, using the vacuum from a water aspirator. The herbicides collected on the cartridges were eluted with 6 ml of acetone by using the vacuum. The eluates were concentrated to 1 ml under a purified nitrogen gas stream. A 10-μl volume of the PEG solution and 5 μl of the internal standard solution were added to each solution and the resulting mixture was analyzed by GC–MS.

The suspended substances, less than 100 mg on glass-fiber filters, were extracted ultrasonically with 24 ml of acetone for 10 min followed by centrifugation at 3000 rpm (1700 g) for 10 min. The extracts (20 ml) were concentrated under reduced pressure at <30°C and the residues were extracted with 3 ml of dichloromethane. The extracts were dried over anhydrous sodium sulfate, and concentrated under reduced pressure at room temperature. The residues were added to 1 ml of acetone, 10 μl of the PEG solution and 5 μl of the internal standard solution for GC–MS analysis.

2.3. GC–MS analytical conditions

GC–MS conditions were as follows: column, a fused-silica column DB-5MS, 0.25 μm film thickness, 30 m×0.32 mm I.D. (J & W); column temperature programmed from 50°C (held for 1 min) to 200°C at a rate of 20°C min^{-1}, then to 280°C (held for 1.5 min) at a rate of 10°C min^{-1}; injector temperature, 250°C; injection mode, splitless; carrier gas pressure, from 0.014 MPa to 0.1 MPa (held for 0.5 min) at a rate of 68 MPa min^{-1}, then back to 0.014 MPa at the same rate; ionization current, 350 μA; electron energy, 70 eV. The selected ions for quantification of the herbicides are listed in Table 1, together with the molecular masses of the herbicides

Table 1
Selected ions for MS determination of herbicides

Herbicide	M_r [a]	m/z		I
ACN	207.6	207	172	1974
Alachlor	269.8	160	188	1903
Benfluralin	335.3	292	264	1672
Bifenox	342.1	341	173	2505
Bromobutide	312.2	120	232	1887
Bromobutide-debromo	233.4	120	233	1697
Butachlor	311.9	160	176	2129
Butamifos	332.4	200	286	2145
Chlomethoxyfen	314.1	313	266	2435
Chlornitrofen	318.5	317	236	2326
Chlorpropham	213.7	127	213	1664
Dimepiperate	263.4	112	146	2088
Dimethametryn	255.4	212	213	2060
Dithiopyr	401.4	286	237	1925
Esprocarb	265.4	222	162	1967
MCPA-ethyl	228.6	228	155	1635
MCPA-thioethyl	244.7	244	125	1835
Mefenacet	298.4	192	120	2575
Molinate	187.3	126	187	1551
Naproanilide	291.4	291	144	2157
Oxadiazon	345.2	175	302	2186
Pendimethalin	281.3	252	162	2044
Piperophos	353.5	140	320	2469
Pretilachlor	311.9	238	262	2173
Prometryn	241.4	241	184	1920
Simazine	201.7	201	186	1748
Simetryn	213.3	213	170	1910
Thiobencarb	257.8	257	100	1983
Trifluralin	335.5	306	264	1666
1,4-Diiodbenzene[b]	329.9	330	203	1450
9-Bromoanthracene[b]	257.1	256	258	2140

[a] Cited from [19] and [20].
[b] Internal standard.

[19,20]. I values were calculated by using the following equation [21,22]:

$$I_A = 100N + 100(\log t_A - \log t_N)/(\log t_{N+1} - \log t_N)$$

where I_A is the I value of compound A, t_A is the retention time of compound A, and t_N and t_{N+1} are the retention times of the n-alkanes bracketing compound A with carbon numbers N and $N+1$. I values for the herbicides and the internal standards are also shown in Table 1.

2.4. Sample collection

Water samples were collected at three sites (Sites 1–3) from the Shinano River in Niigata Prefecture, Japan. The river is the longest river in Japan. Site 1 is situated at the mouth of the river; Sites 2 and 3 are located 14 and 25 km upstream from the river mouth, respectively. The amounts of herbicides used annually in the prefecture were 8100–8500 tons in cultivated areas and 340–350 tons in non-cultivated areas during the fiscal years 1991 to 1993.

The surface water was sampled in a 1-l glass bottle at Sites 1–3 from May to November 1995. Samples were also taken in April 1995 from Site 2. The collected samples were processed within 24 h of collection.

3. Results and discussion

3.1. GC–MS analytical conditions

Fig. 1 shows a total ion chromatogram of the standard herbicides and the internal standards with the PEGs. Most of the highest peaks are those of PEGs which we added to herbicide standards and samples so that the herbicides provide sharp peaks [18,23]. Some peaks of PEGs did not separate from those of the target compounds, such as dimethametryn. The PEGs, however, gave no fragment ions of m/z 100 or more, except for m/z 101, 103, 104 and 119. Therefore, we selected the ions for the herbicide determination avoiding those from PEGs. In particular, bromobutide, bromobutide-debromo and dimepiperate, which have the most abundant ion of m/z 119, were determined without the interference

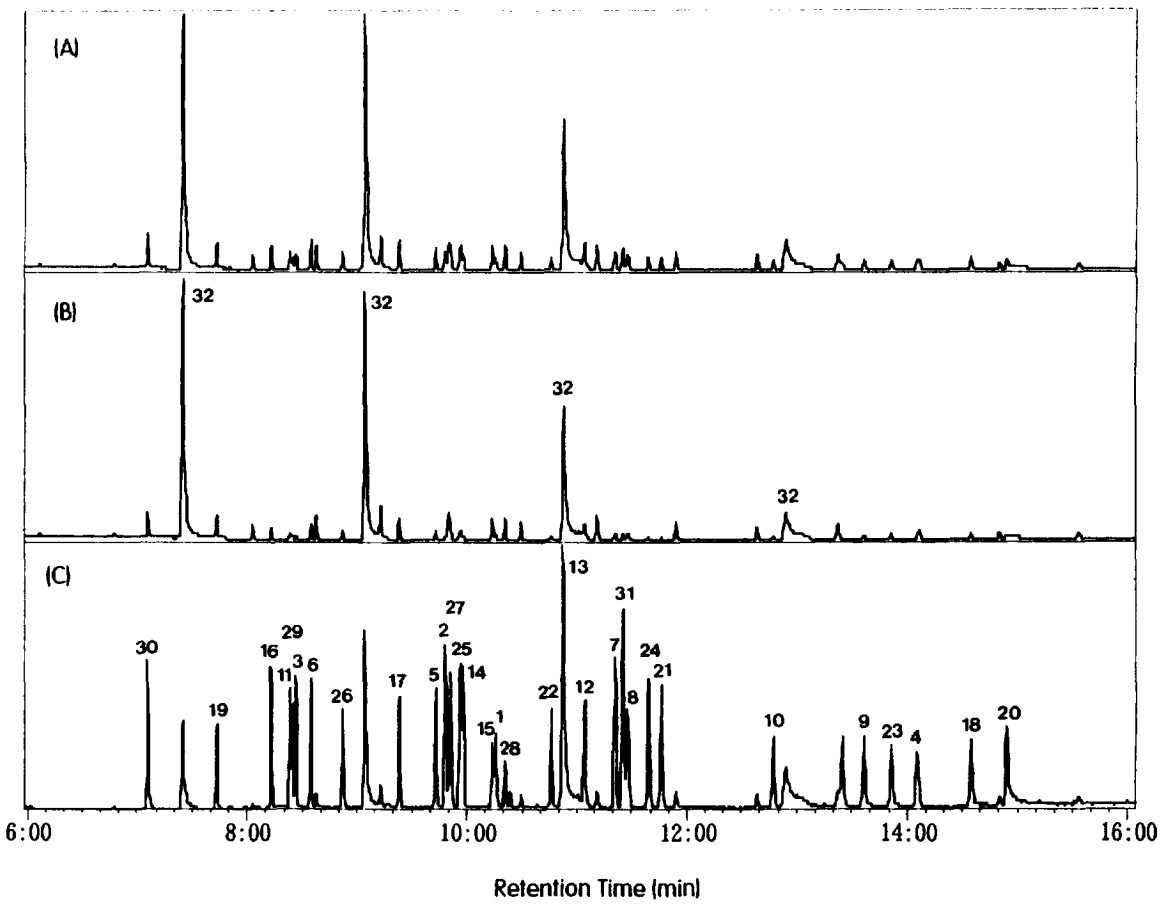

Fig. 1. Total ion chromatogram of herbicides and internal standards. (A) Scan *m/z* 50–450. (B) Scan *m/z* 50–100. (C) Scan *m/z* 100–450. Peaks: 1 = ACN; 2 = alachlor; 3 = benfluralin; 4 = bifenox; 5 = bromobutide; 6 = bromobutide debromo form; 7 = butachlor; 8 = butamifos; 9 = chlomethoxyfen; 10 = chlornitrofen; 11 = chlorpropham; 12 = dimepiperate; 13 = dimethametryn; 14 = dithiopyr; 15 = esprocarb; 16 = MCPA-ethyl; 17 = MCPA-thioethyl; 18 = mefenacet; 19 = molinate; 20 = naproanilide; 21 = oxadiazon; 22 = pendimethalin; 23 = piperophos; 24 = pretilachlor; 25 = prometryn; 26 = simazine; 27 = simetryn; 28 = thiobencarb; 29 = trifluralin; 30 = 1,4-diiodobenzene; 31 = 9-bromoanthracene; 32 = PEGs.

by using *m/z* 120 and 232, 120 and 233, and 112 and 146, respectively (Table 1).

Among the investigated herbicides, chlorpropham ($I = 1664$) and trifluralin ($I = 1666$) were only incompletely separated in the total ion chromatogram (Fig. 1); prometryn ($I = 1920$) and dithiopyr ($I = 1925$), esprocarb ($I = 1967$) and ACN ($I = 1974$), and butamifos ($I = 2145$) and an internal standard 9-bromoanthracene ($I = 2140$) were unsatisfactorily resolved, respectively. We, therefore, selected ions for the determination comparing the mass spectra of the herbicides and the internal standard. Thereby, these compounds can be determined without interfering with each other by using the ions given in Table 1. Moreover, I of simetryn, 1910, was almost the same as that of carbaryl, 1913, and esprocarb had the same I of 1967 as malathion and probenazole; dimetametryn ($I = 2060$) was incompletely separated from isofenphos ($I = 2067$). Nevertheless, the selected ions (Table 1) for the target herbicides were not interrupted by these insecticides nor by the fungicide. Consequently, the investigated herbicides were separated within 18 min under the GC–MS conditions described in Section 2.3.

Although a few pesticides have been determined accurately by using the stable-labeled pesticides as

internal standards [7,9], the isotope dilution is not proper for determining many herbicides simultaneously. Several stable-labeled isotopes of polycyclic aromatic hydrocarbons, such as [$^2H_{10}$]anthracene, [$^2H_{12}$]chrysene, [$^2H_{10}$]fluoranthene, [$^2H_{10}$]pyrene and [$^2H_{10}$]phenanthrene, and have been used as internal standards for the simultaneous determination of pesticides [13,23]. However, these compounds have few characteristic ions except for their base peaks. Thus, additional ions are appropriate to give a high probability of identification. On the other hand, some halogenated compounds, such as 1,2-dibromopropane [24] and 2-bromo-1-chloropropane [25], have been used as internal standards for GC–MS determination of volatile organic compounds. Brominated and/or chlorinated compounds give characteristic peaks. Therefore, we selected 9-bromoanthracene and 1,4-diiodobenzene [18] as internal standards to determine the herbicides. The halogenated compounds give characteristic fragment ions with satisfactory intensity and proper I values.

The ratios of peak areas of the selected ions to those of the internal standards were used for quantification of herbicides. The herbicides with $I<2000$ and those with $I>2000$ were determined using 1,4-diiodobenzene and 9-bromoanthracene as the internal standard, respectively. Calibration curves were linear ($r>0.996$) over 0.04 to 8 ng for bifenox, chlomethoxyfen, chlornitrofen and pendimethalin, and 0.02 to 8 ng for the other herbicides.

3.2. Recoveries of herbicides from water

Extraction efficiencies for the 29 herbicides from the cartridges were determined by passing 50 ml of distilled water spiked with 3 μg of the herbicide through cartridges. The cartridges were washed with 10 ml of distilled water and were air-dried, then the herbicides were eluted from the cartridge using different solvents, such as methanol, ethyl acetate and acetone. Hexane and dichloromethane following acetone were also investigated as elution solvents. The results are given in Table 2. A 6-ml volume of acetone was the recommended solvent for the elution of the herbicides from the cartridge.

Recoveries of the herbicides from 500 ml of filtered river water were determined by adding 0.25 μg of the herbicides to the waters as an acetone solution, stirring the waters for 30 min, and extracting the herbicides from the waters using a series of two cartridges each under the conditions described in Section 2. The results are shown in Table 2. No herbicide was detected from the second cartridge. Recoveries from the filtered river water were good (81.6–128%). The relative standard deviation was 0.40–10%.

Johnson et al. [8] reported that dissolved organic material decreased the extraction recoveries of pesticides from water samples. Nevertheless, four herbicides, benfluralin, chlornitrofen, pendimethalin and trifluralin, gave good recoveries of more than 80% from filtered river water, although less than 75% of them were eluted from the cartridge (Table 2). Improvements in the recoveries from river water were also observed for the other herbicides, such as ACN, esprocarb and simetryn. Okumura [23] found that coextracts from environmental samples passivated the activated surfaces in GC and provided sharper, more symmetric peaks for some pesticides than those in standard solution. Holland et al. [26] reported pesticide analyses in wine and suggested that more polar, less stable, pesticides gave recoveries in excess of 100%, because of coextractives conferring a protective effect during GC analysis of the pesticides. Therefore, the increases in recoveries of the herbicides in our results could have been caused predominantly by coextractives from river water.

The minimum detectable concentrations [27] were 0.02 $\mu g\ l^{-1}$ for bifenox, chlomethoxyfen, chlornitrofen and pendimethalin, and 0.01 $\mu g\ l^{-1}$ for the other herbicides.

3.3. Recoveries of herbicides from suspended substances

Extraction efficiencies for the herbicides from suspended substances were determined by adding 3 μg or 0.25 μg of the herbicides as an acetone solution to suspended substances on the glass fiber filter from river water. Allowing the filter to stand for 20 min in order to evaporate the acetone, the herbicides were extracted from the filter as described in Section 2. Methanol, hexane, ethyl acetate, dichloromethane and acetone were investigated as

Table 2
Desorption efficiencies from the solid-phase and overall recoveries of herbicides

Herbicide	Desorption efficiency (%)										Recovery from filtered river water[e] (%)	
	Methanol		Ethyl acetate		Acetone							
	3 ml	6 ml	3 ml	6 ml	3 ml		3 ml + HX[c]	3 ml + DCM[d]	6 ml			
					Mean[a]	R.S.D.[b]			Mean[a]	R.S.D.[b]	Mean[a]	R.S.D.[b]
ACN	68.9	68.9	78.3	78.3	74.6	8.4	74.6	74.6	81.9	12	128	14
Alachlor	67.7	67.7	80.5	80.5	80.1	7.4	80.1	80.1	101	6.1	105	3.4
Benfluralin	48.1	48.1	73.4	73.4	55.0	13	69.6	70.3	67.9	1.8	83.6	2.2
Bifenox	<5	<5	78.3	78.3	69.2	9.1	69.2	79.0	92.9	8.2	98.1	5.7
Bromobutide	77.1	77.1	78.2	78.2	80.1	8.5	80.1	80.1	103	2.7	108	3.9
Bromobutide-debromo	76.4	76.4	76.6	76.6	79.5	7.8	79.5	79.5	92.7	7.8	101	7.1
Butachlor	50.6	64.0	79.6	79.6	73.4	9.3	83.5	83.1	100	5.2	112	1.1
Butamifos	73.9	73.9	81.4	81.4	81.2	9.2	81.2	81.2	96.5	3.9	104	2.6
Chlomethoxyfen	<5	<5	74.9	74.9	70.9	5.9	70.9	83.2	91.3	8.7	97.9	6.7
Chlornitrofen	<5	<5	77.8	77.8	63.2	13	70.6	80.5	71.9	3.2	81.6	4.4
Chlorpropham	57.5	57.5	81.1	81.1	68.2	5.1	68.2	79.1	95.7	5.4	103	4.6
Dimepiperate	<5	42.2	80.1	80.1	71.7	7.8	84.0	85.8	104	8.9	110	4.8
Dimethametryn	64.5	64.5	83.1	83.1	79.4	6.9	79.4	79.4	96.4	3.2	105	5.8
Dithiopyr	73.5	73.5	79.5	79.5	74.4	6.6	74.4	82.4	84.1	8.6	85.9	5.0
Esprocarb	<5	35.9	76.2	76.2	63.4	13	77.5	78.3	87.3	3.6	94.1	0.23
MCPA-ethyl	22.5	47.3	72.6	72.6	57.9	12	70.3	74.8	89.7	5.8	89.3	5.3
MCPA-thioethyl	<5	<5	76.6	76.6	57.9	14	74.8	82.6	98.1	4.0	98.9	6.5
Mefenacet	<5	55.4	78.2	78.2	82.5	2.5	82.5	82.5	90.7	2.9	103	12
Molinate	25.8	45.9	76.8	76.8	64.1	9.7	75.9	80.5	90.8	7.0	98.7	6.2
Naproanilide	<5	60.0	76.8	76.8	79.8	2.4	79.8	79.8	96.0	3.1	103	9.5
Oxadiazon	38.0	59.4	76.1	76.1	70.8	6.7	83.2	84.0	93.2	1.8	96.8	1.6
Pendimethalin	<5	42.9	92.6	92.6	71.1	8.9	86.4	86.5	73.2	7.3	86.4	2.8
Piperophos	54.1	71.8	79.9	79.9	85.9	5.7	85.9	85.9	93.5	5.3	100	9.1
Pretilachlor	64.1	64.1	78.5	78.5	79.8	8.6	79.8	79.8	108	6.5	112	2.7
Prometryn	70.9	70.9	79.4	79.4	82.8	8.2	82.8	82.8	93.6	4.5	101	4.1
Simazine	84.6	84.6	78.1	78.1	78.9	11	78.9	78.9	102	9.6	112	7.3
Simetryn	78.8	78.8	77.9	77.9	80.4	9.2	80.4	80.4	93.5	9.4	120	11
Thiobencarb	<5	30.7	80.3	80.3	64.4	13	77.6	80.6	97.6	5.1	110	0.63
Trifluralin	50.3	50.3	76.8	76.8	57.3	13	71.1	72.3	72.1	1.2	87.1	5.8

[a] Percentage mean recovery ($n = 3$).
[b] Percentage relative standard deviation.
[c] A 3-ml volume of hexane.
[d] A 3-ml volume of dichloromethane.
[e] The herbicides collected on the cartridges were eluted with 6 ml of acetone.

extraction solvents. The results are shown in Table 3. Acetone was the recommended solvent for the extraction of the herbicides from suspended substances. The recoveries of the target compounds were good (80–110%).

The minimum detectable concentrations [27] were 0.1 $\mu g\ g^{-1}$ for bifenox, chlomethoxyfen, chlornitrofen and pendimethalin, and 0.05 $\mu g\ g^{-1}$ for the other herbicides.

3.4. Monitoring of herbicides in river water

This method was applied to the monitoring of herbicides in river water from the Shinano River. Nine herbicides, bromobutide, butachlor, dimepiperate, esprocarb, mefenacet, molinate, pretilachlor, simetryn and thiobencarb were detected from some filtered water samples. Four herbicides, dimepiperate, esprocarb, mefenacet and pretilachlor, were detected from some of the suspended substances. Typical chromatograms of the detected herbicides of standards and samples are shown in Fig. 2. Every herbicide could be determined well without interferences.

Concentration variations in the sum of the detected herbicides in soluble and suspended phases are given in Table 4. While butachlor was detected only in May, the other eight herbicides were detected from

Table 3
Recoveries of herbicides from suspended substance

Herbicide	Recovery (%)					
	Methanol[a]	Hexane[a]	Ethyl acetate[a]	Dichloromethane[a]	Acetone[b]	
					Mean	R.S.D.
ACN	81.3	52.9	88.3	82.9	110	2.5
Alachlor	75.3	79.1	85.6	83.2	102	3.9
Benfluralin	73.2	81.3	78.7	88.0	90.5	13
Bifenox	54.7	84.8	104	83.5	95.6	12
Bromobutide	73.2	80.3	81.7	86.5	99.5	2.3
Bromobutide-debromo	65.3	69.3	74.7	80.4	101	3.2
Butachlor	79.2	79.9	91.1	81.1	93.9	9.1
Butamifos	89.1	82.9	94.5	77.1	93.1	7.8
Chlomethoxyfen	79.3	70.3	87.7	76.8	96.0	9.0
Chlornitrofen	84.9	85.5	97.7	83.2	100	6.0
Chlorpropham	69.6	77.1	84.0	85.2	96.7	2.7
Dimepiperate	90.8	84.0	88.9	87.1	96.9	6.2
Dimethametryn	76.4	70.0	4.3	88.8	104	1.2
Dithiopyr	86.0	82.5	85.5	86.1	86.5	13
Esprocarb	87.6	81.6	84.4	80.8	93.3	7.9
MCPA-ethyl	68.0	74.9	70.7	83.3	80.0	1.7
MCPA-thioethyl	57.9	81.5	82.3	87.7	82.8	5.2
Mefenacet	84.9	45.2	94.4	80.8	103	1.8
Molinate	78.9	79.7	74.7	90.7	90.3	1.8
Naproanilide	86.1	73.3	112	92.9	104	5.3
Oxadiazon	75.1	83.7	84.9	82.5	89.6	12
Pendimethalin	83.7	80.1	83.4	75.4	94.6	11
Piperophos	77.1	58.3	92.0	74.4	94.1	5.7
Pretilachlor	74.8	74.4	86.5	74.7	97.1	8.8
Prometryn	75.2	71.3	86.5	81.6	97.7	2.0
Simazine	71.5	51.9	78.8	82.3	101	0.23
Simetryn	76.5	40.0	78.7	70.0	101	6.8
Thiobencarb	70.9	83.6	86.7	87.1	101	3.5
Trifluralin	76.4	82.3	85.7	89.6	92.9	14

[a] Spiked with 3 μg.
[b] Spiked with 0.25 μg ($n=3$).

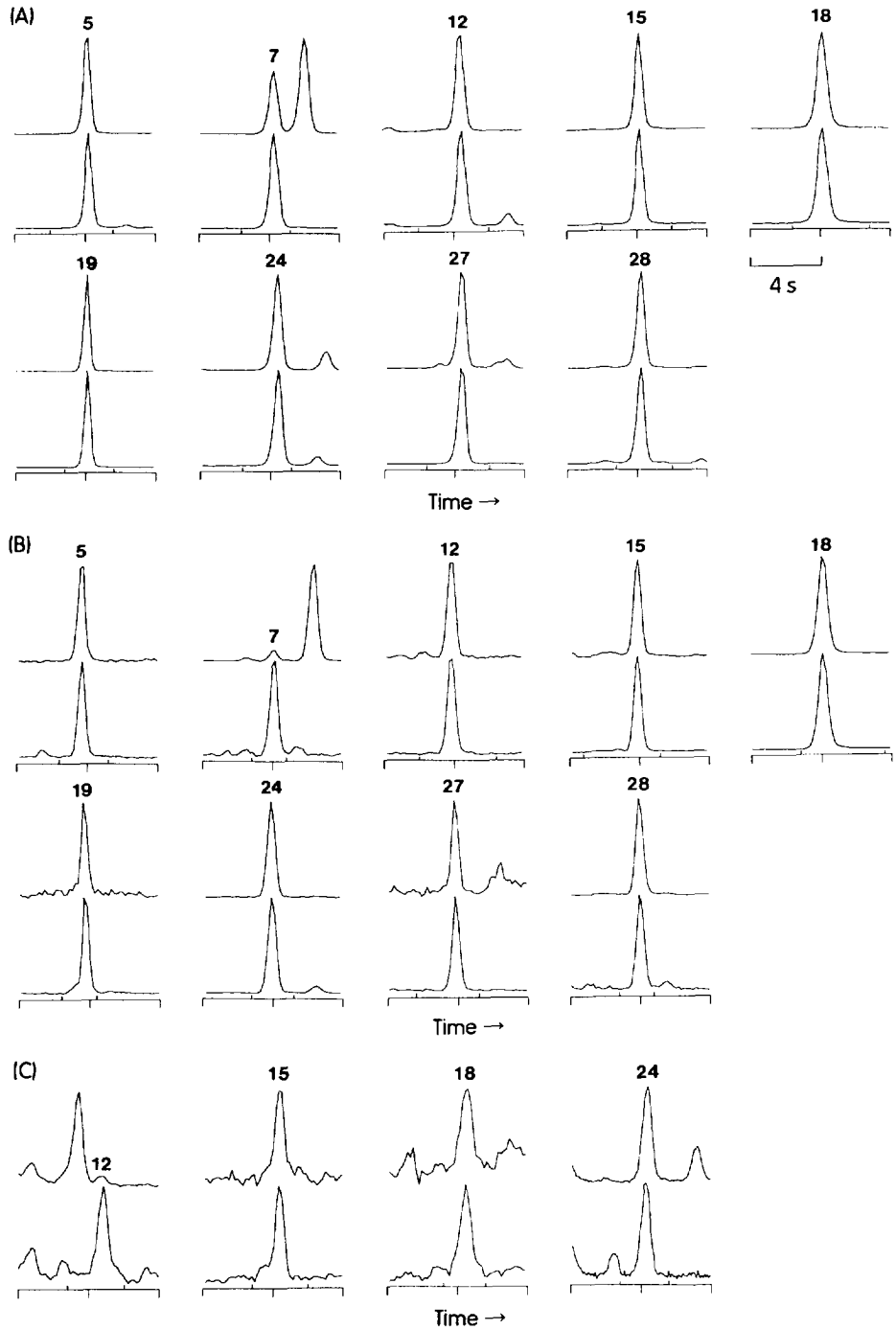

Fig. 2. Mass chromatograms of herbicides detected in river water. (A) Standard. (B) Filtered river water. (C) Suspended substances. Peaks (retention time, m/z of upper row and m/z of lower row): 5 = bromobutide (9.72 min, 232 and 120); 7 = butachlor (11.35 min, 176 and 160); 12 = dimepiperate (11.07 min, 146 and 112); 15 = esprocarb (10.23 min, 162 and 222); 18 = mefenacet (14.58 min, 120 and 192); 19 = molinate (7.72 min, 187 and 126); 24 = pretilachlor (11.65 min, 262 and 238); 27 = simetryn (9.85 min, 170 and 213); 28 = thiobencarb (10.35 min, 100 and 257).

Table 4
Herbicide concentrations in river water

Site	Herbicide	Concentration ($\mu g\ l^{-1}$)							
		April	May	June	July	August	September	October	November
1	Bromobutide	–	0.80	0.46	0.03	<0.01	<0.01	<0.01	<0.01
	Butachlor	–	0.11	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Dimepiperate	–	0.79	0.22	<0.01	0.05	<0.01	<0.01	<0.01
	Esprocarb	–	0.65	0.07	0.02	<0.01	<0.01	<0.01	<0.01
	Mefenacet	–	1.9	0.38	0.06	<0.01	<0.01	<0.01	<0.01
	Molinate	–	0.15	0.62	0.05	<0.01	<0.01	<0.01	<0.01
	Pretilachlor	–	1.6	0.06	<0.01	<0.01	<0.01	<0.01	<0.01
	Simetryn	–	0.06	0.47	0.09	0.03	<0.01	<0.01	<0.01
	Thiobencarb	–	0.05	0.29	0.05	<0.01	<0.01	<0.01	<0.01
2	Bromobutide	<0.01	0.35	0.45	0.03	<0.01	<0.01	<0.01	<0.01
	Butachlor	<0.01	0.09	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Dimepiperate	<0.01	0.78	0.09	0.03	<0.01	<0.01	<0.01	<0.01
	Esprocarb	<0.01	0.52	0.05	<0.01	<0.01	<0.01	<0.01	<0.01
	Mefenacet	<0.01	1.8	0.36	0.05	<0.01	<0.01	<0.01	<0.01
	Molinate	<0.01	0.16	0.41	0.05	<0.01	<0.01	<0.01	<0.01
	Pretilachlor	<0.01	1.2	0.06	0.02	<0.01	<0.01	<0.01	<0.01
	Simetryn	<0.01	0.06	0.44	0.07	0.03	<0.01	<0.01	<0.01
	Thiobencarb	<0.01	0.05	0.28	0.04	<0.01	<0.01	<0.01	<0.01
3	Bromobutide	–	0.15	0.32	0.02	<0.01	<0.01	<0.01	<0.01
	Butachlor	–	0.08	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Dimepiperate	–	0.26	0.09	<0.01	<0.01	<0.01	<0.01	<0.01
	Esprocarb	–	0.22	0.05	<0.01	<0.01	<0.01	<0.01	<0.01
	Mefenacet	–	0.92	0.21	0.03	<0.01	<0.01	<0.01	<0.01
	Molinate	–	0.06	0.39	0.05	<0.01	<0.01	<0.01	<0.01
	Pretilachlor	–	0.85	0.05	<0.01	<0.01	<0.01	<0.01	<0.01
	Simetryn	–	0.03	0.37	0.04	0.03	<0.01	<0.01	<0.01
	Thiobencarb	–	0.05	0.26	0.06	<0.01	<0.01	<0.01	<0.01

May to July or August. During this period, these herbicides were applied to cultivated areas including paddy fields as well as to non-cultivated areas in Niigata Prefecture. Maximum concentrations were 0.11 $\mu g\ l^{-1}$ of butachlor at Site 1 to 1.9 $\mu g\ l^{-1}$ of mefenacet at Site 1. Mean concentrations of the herbicides at Site 1 were higher than those at the other sites. No herbicides were detected during September to November at any of the sites.

The ratios of the four herbicides detected both in the soluble phase and in the suspended phase are summarized in Table 5. The ratio of the herbicides in the suspended phase ranged from 0.4% (dimepiperate) to 2.3% (esprocarb).

Table 5
Ratio of herbicides in the soluble phase and the suspended phase in riverine water samples

Herbicide	Ratio (%)	
	Soluble phase	Suspended phase
Dimepiperate	99.6	0.4
Esprocarb	97.7	2.3
Mefenacet	99.3	0.7
Pretilachlor	99.3	0.7

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