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Advanced analytical determination of volatile organic compounds (VOC) and other major contaminants in water samples using GC-Ion Trap MS

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Abstract: The GC-Ion Trap MS is recently one of the most efficient instrumental analysis recommended for understanding the chemistry of volatile organic compounds, not only in water but even in the food chain and other environmental media (air and soil). Results of the experiment conducted on water samples from Kuguri and Yatsutani sampling stations showed considerably higher levels of organic enrichment (COD = 10 mg/L and 11 mg/L respectively). Total concentrations of Pb (0.072 mg/L and 0.093 mg/L) and Cd (0.004 mg/L and 0.011 mg/L) on the other hand, invariably exceeded the maximum allowable concentrations for human health and the living environment (Pb = 0.005 mg/L; Cd = 0.001 mg/L respectively). And the toxicity levels for these contaminants at LC_{50} showed critical impact on rainbow trout (hypersensitive species) at 0.14 mg/L for Pb and 0.007 mg/L for Cd in 96 hours respectively. Although these major contaminants including phenol and 3-, 4-cresol, showed relatively higher toxicity impact in the experimental media, it would remain contentious to justify any associated potential dangers without regular routine water monitoring, at least for a period of one year. Nevertheless, the data could serve as a benchmark through which other phenomena can easily be investigated.

Key words: volatile organic compounds (VOC); major contaminants; simultaneous analysis; GC/Ion Trap MS; water quality

Introduction

Significant water quality management for mitigation of environmental pollution caused by hazardous chemicals is still a matter of stringent environmental consideration in Japan. Subsequently, regular on-going monitoring are implemented, especially for synthetic chemicals such as herbicides and pesticides often used as farm chemicals, and mostly belonging to the class of VOC (Andrews, 1997; ANS, 1999; EHD, 1991). Although the basic environmental laws have established restrictions on the disposal of VOC in the aquatic environment, even a minimum impact in the living environment aesthetically develops the contention of citizens' perception of the past for a possible discharge of these effluents into the water body. The minamata disease incident and frequently reported heavy metal pollution in aquatic ecosystems during the early 1970s still remained in chemical literature as imminent examples of the legacy of industrial decay in Japan. Against these backdrops, an analytical method for simultaneous determination of VOC in water by use of GC-Ion Trap MS has been developed recently with very high sensitivity and precision quality (Kadokami, 1995). Many simultaneous analytical methods have been developed in Japan for monitoring of chemicals in environmental media, but the GC-Ion Trap MS has been widely accepted as the most suitable instrumental technique due to its high sensitivity and high identifiable ability (Kadokami, 1991; Kenmotsu, 1993; Suzuki, 1992).

This investigation was carried out to substantiate the fate of over 200 VOC in water samples from Kuguri and Yotsutani sampling station after a report of sudden fish kill. Also taking into consideration was other limiting factors such as COD, heavy metals, phenols, etc., that are also capable of causing incidental fish kills, especially in migratory hypercritical fish.

1 Materials and methods

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The investigation was carried out in three consecutive months (January-March, 1999) at the Aqua Research Center, Kitakyushu Institute of Environmental Sciences, Tobata, Kitakyushu City, Japan during a laboratory training program.

The GC-Ion Trap MS method was used for simultaneous analysis of VOC mostly pesticides in accordance with the recent analytical procedure developed (Kadokami, 1995). Extraction procedures for samples prepared for GC-Ion Trap MS analysis and other parameters such as heavy metals (Pb, Zn, Cu, Cd, Cr^{6+}), COD, phenol, etc., followed the standard methods for the examination of water and wastewater (Standard methods for the examination of water and wastewater, 1992).

Fig 1 shows the extraction procedure for VOC in the samples. Toxicity evaluation for the major contaminants analyzed was based on the median tolerance limit (TL_m) test, also called as LC_{50} using moving average method to calculate log concentrations in an attempt to ascertain the lethal concentrations of these potential hazardous chemicals in the samples analyzed (MBLI, 1999; Biology of Water Pollution, 1999; Exxon Company, 1997).

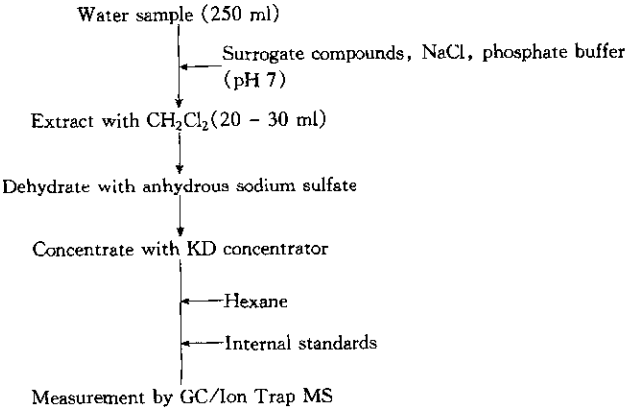

Fig. 1 Analytical flow sheet for extraction VOC and other major contaminants

2 Extraction procedure

250 ml of water from each of the Kuguri and Yatsutani samples was collected in a glass bottle and transferred into a separating funnel. 2.5 μl of the mixed surrogate solution and 10g of sodium chloride were added to the sample. 20—30 ml of dichloromethane was added into the bottle to rinse the wall, and then transferred into a separating funnel. Extraction was carried out with a mechanical shaker for 10 min. The extraction procedure was repeated with another 20—30 ml of dichloromethane. After the second extraction, the pH of the sample solution was adjusted below 2 using 6 mol/L HCl. The acidified sample was again extracted with another 20 – 30 ml of dichloromethane. After the third extraction, the pH of the sample was adjusted above 11 with a 6 mol/L NaOH solution. The alkalized aqueous phase was extracted with another 50 ml of dichloromethane. Each extract was combined and dehydrated by passing it through a column packed with anhydrous sodium sulfate (7 ml), and concentrated to few ml in a Kuderna-Danish (KD) concentrator. Haxane (1.0 ml) was added to further purify the concentrate and re-concentrated to 1.0 ml. Prior to the GC-Ion Trap MS measurement, 40 μl of the mixed internal standard solution was added to the concentrate, and finally, 1 ml aliquot of the concentrate was injected into the column using an auto-sampler.

3 TL_m testing method

Median tolerant level (TL_m) or lethal concentration of poisoning (LC_{50}) in fish is widely considered as an index of fish kill in acute or chronic poisoning of aquatic organisms. The value however, is determined according to the experimental objectives. In this study, the concentration of each substance that may have caused 50% death of the hypercritical fish in question within a constant period of time (24, 48, 96 hours) was the approach employed to determine the survival percentage/lethal concentrations of the major contaminants.

The TL_m test therefore, was based on the following conditions, not taking into account the density of each substance (dose) injected into the experimental organism resulting to 50% death in a given period of time (LD_{50}):

· Fish selected for the toxicity test should be prepared at least one week or preferably 10 days before the LC_{50} determination in order to adapt them to the water temperature condition and other characteristics of the experimental medium. During this preparation, normal feeding should be done only once daily, and no feeding two days before the testing.

· Species used for the experiment must have been raised in the same environment, and preferable length of species is about 75 mm and the size of the largest fish should not exceed 1.5 times that of the smallest.

· Comparing the general characteristics of the receptor during the testing period, the water temperature must be the same, and the number of fish per unit area should be at least 10, depending on the size of the receptor. In other words, each receptor must be capable of accommodating 2g of fish per liter.

· Use only fish with symptoms of anomalies or no survival 4 days before the LC_{50} calculation. If majority of the fish remain alive in a period of 48—96 hours then the potential toxicity is at larger concentration, and if majority of the fish died in 24 hours then potential toxicity is at lower concentration of the index determined. Results are interpreted in log concentrations to show the lethal effect of each contaminant analyzed.

4 Results and discussion

Water quality assessment still remains a crucial issue for human safety and the protection of our living environment, especially when polluted by synthetic chemicals such as herbicides, pesticides and other chemicals from commercial products of industrialization, widely classified as VOC.

In quantitative terms, evaluation of organic pollutants (VOC) in the water samples based on the maximum standard limits for water quality in Kitakyushu Environment are shown in Table 1. Among the VOC analyzed, phenol, 3-, 4-cresol, 4-cymene, diethyl phthalate and bis (2-diethylhexyl) phthalate levels from the GC-Ion Trap MS analysis were relatively higher (one to several $\mu g/L$). All the other VOC were below the maximum allowable concentrations for Kitakyushu rivers recommended for fish production. However, further investigation to substantiate the incidental impacts for water quality conditions would require regular routine monitoring for at least a period of one year.

Table 1 Results of VOC analysis in the water samples

No.	VOC analyzed	Blank	Kuguri	Yotsutani	MDL, $\mu g/L$	Use and toxicity data	LC_{50}
1	n-$C_{13}H_{28}$	0.014	0.064	0	0.001		
2	n-$C_{14}H_{30}$	0	0.039	0.037	0.002		
3	n-$C_{15}H_{32}$	0.013	0.241	0.059	0.002		
4	n-$C_{16}H_{34}$	0	0.089	0.092	0.001		
5	n-$C_{17}H_{36}$	0	0.149	0.09	0.002		
6	n-$C_{18}H_{38}$	0.02	0.128	0.048	0.001		
7	n-$C_{19}H_{40}$	0	0.045	0.04	0.002		
8	n-$C_{20}H_{42}$	0	0.06	0.044	0.002		
9	n-$C_{21}H_{44}$	0	0.048	0.036	0.003		
10	n-$C_{22}H_{46}$	0	0.047	0.039	0.004		
11	n-$C_{23}H_{48}$	0	0.044	0.037	0.008		
12	n-$C_{24}H_{50}$	0	0.064	0.063	0.01		
13	n-$C_{25}H_{52}$	0	0.07	0.058	0.02		
14	n-$C_{26}H_{54}$	0	0.052	0	0.025		
15	Squalane	0.012	0.524	0.14	0.025		
16	n-$C_{27}H_{56}$	0	0.027	0.014	0.03		

Table 1 (cont'd)

No.	VOC analyzed	Blank	Kuguri	Yotsutani	MDL, μg/L	Use and toxicity data	LC_{50}
17	n-$C_{28}H_{58}$	0	0	0	0.03		
18	n-$C_{29}H_{60}$	0	0	0	0.03		
19	n-$C_{30}H_{62}$	0	0	0	0.035		
20	n-$C_{31}H_{64}$	0	0	0	0.04		
21	n-$C_{32}H_{66}$	0.002	0.005	0	0.04		
22	Pentachloroethane	0	0	0	0.002		
23	Hexachloroethane	0	0	0	0.001		
24	1,2-dibromo-3-chloropropane	0	0	0	0.001		
25	Hexachlorobutadiene	0	0	0	0.001		
26	Styrene	0	0	0	0.001	Manuf. of styrol, poly-styrene resin, etc.	
27	4-cymene	0.103	2.031	0.499	0.001		
28	Pentamethylbenzene	0	0	0	0.002		
29	1,3-dichlobenzene	0	0.27	0.016	0.001		
30	Benzylchloride	0	0	0	0.001	Solvent for O. T. intermediate of dyestuff	
31	1,4-dichlobenzene	0	0.088	0.097	0.001	Int. of dyestuff insecticide, for O. T.	
32	1,2-dichlobenzene	0.006	0.056	0.48	0.001	Organic solvent, insecticide, conductor of heat	
33	3-bromochlorobenzene	0	0	0	0.002		
34	2-bromochlorobenzene	0	0	0	0.001		
35	1,3,5-trichlorobenzene	0	0	0	0.001		
36	1,2,4-trichlorobenzene	0	0	0	0.001		
37	Hexachloropropylene	0	0	0	0.001		
38	1,2,3-trichlorobenzene	0	0	0	0.001		
39	1, 2, 4, 5-tetrachlorobenzene	0	0	0	0.001		
40	Pentachlorobenzene	0	0	0	0.001		
41	Hexachlorobenzene	0	0	0	0.001		
42	Naphthalene	0	0.069	0.069	0.001		
43	2-methylnaphthalene	0	0.015	0.014	0.001	Manuf. of vitamin K3	
44	Biphenyl	0	0.006	0.007	0.001		
45	2,6-dimethylnaphthalene	0	0.011	0.01	0.001		
46	1,3-dimethylnaphthalene	0	0.012	0.013	0.001		
47	Diphenylmethane	0	0	0	0.001		
48	1,4-dimethylnaphthalene	0	0	0.005	0.001		
49	2,3-dimethylnaphthalene	0	0	0.006	0.001	Generated by combust of organic matter, exists in tabaco smoke	
50	Acenaphthylene	0	0.01	0.011	0.001		
51	1,2-dimethylnaphthalene	0	0	0	0.001		
52	2-isopropylnaphthalene	0	0	0	0.002		
53	1,8-dimethylnaphthalene	0	0	0	0.001		
54	Acenaphthene	0	0	0	0.001		
55	Fluorene	0	0.007	0.009	0.001		

Table 1 (cont'd)

No.	VOC analyzed	Blank	Kuguri	Yotsutani	MDL, μg/L	Use and toxicity data	LC_{50}
56	2,6-diisopropyl-naphthalene	0	0	0	0.001		
57	Phenanthrene	0	0.017	0.023	0.001	Material for synthesis of anthraquinone-dye	
58	Anthracene	0	0	0	0.001		
59	1-phenylnaphthalene	0	0	0	0.001		
60	2-terphenyl	0	0	0	0.001		
61	4,5-mehtylene-phenanthrene	0	0	0	0.001		
62	2-phenylnaphthalene	0	0	0	0.001		
63	1,8-dimethylphenan-threne	0	0.006	0.005	0.001		
64	Fluoranthene	0	0.005	0.005	0.001		
65	Pyrene	0	0	0	0.001		
66	3-terphenyl	0	0	0	0.001		
67	4-terphenyl	0	0	0	0.001		
68	2,3-benzofluorene	0	0	0	0.002		
69	Benzo(a)anthracene	0	0	0	0.001		
70	Chrysene	0.043	0	0	0.001		
71	Triphenylene	0	0	0	0.001		
72	Benzo(b)fluoranthene	0	0	0	0.007		
73	7, 12-dimethylbenz (a)-anthracene	0	0	0	0.001		
74	Benzo(I&k) fluoranthene	0	0	0	0.011		
75	Benzo(e)pyrene	0	0	0	0.25		
76	Benzo(a)pyrene	0	0	0	0.02		
77	Perylene	0	0	0	0.02		
78	3-methylcholanthrene	0	0	0	0.034		
79	Indeno (1, 2, 3-cd) pyrene	0.03	0	0	0.01		
80	Dibemzo(a,h)-anthrancene	0	0	0	0.025		
81	Benzo(ghi)perylene	0	0	0	0.02		
82	2-chloronaphthalene	0	0	0	0.001		
83	1-chloronaphthalene	0.013	0	0	0.001	Fungicide, solvent, antiseptic	
84	Dicyclopentadiene	0	0	0	0.001		
85	Trans-decahydrona-phthalene	0	0	0	0.003		
86	Longifolene	0.008	0	0	0.004		
87	Hexachlorocyclopen-tadiene	0	0	0	0.001		
88	1,2,3-trimethoxy-benzene	0	0	0	0.001		
89	Diphenyl ehter	0	0.008	0.006	0.001	Perfume for soap, conductor of heat	
90	Dibenzylether	0	0.105	0.117	0.002	Carrer of dyestuff, perfume, solvent	
91	Bis(2-chloroethyl)-ether	0	0	0	0.002		
92	Bis (2-chloroiso-propyl) ether	0	0	0	0.009		

Table 1 (cont'd)

No.	VOC analyzed	Blank	Kuguri	Yotsutani	MDL, μg/L	Use and toxicity data	LC_{50}
93	Bis-(2-chloroethoxy)-methane	0	0	0	0.001		
94	4-chlorophenyl phenyl ether	0	0	0	0.001		
95	4-bromophenyl phenyl ether	0	0	0	0.001		
96	Acetophenone	0	0	0.221	0.001	Perfume, polymerization catalyst of olefin	
97	Isophorone	0	0.013	0.018	0.001	Mainly for solvent material for kind of compounds	
98	2,6-di-tert-butyl-4-benzoquinone	0.008	0	0	0.003		
99	Anthraquinone	0	0.013	0.019	0.003	Intermediate for anthraquinone-dye synthesis	
100	Benzanthrone	0.067	0	0	0.001		
101	Phenol	0	3.668	4.275	0.001	Local anesthsia for dental treatment, for synthesis of resine, plasticizer	4ppm (rainbow-traut 18h)
102	2-cresol	0	0.139	0.179	0.001	Purifier of lubricating oil	
103	3-,4-cresol	0	6.936	5.568	0.001	Material synth-resin, medicine, plasticizer, pesticide, disinfectant	m-25ppm (crucian carp24)
104	2-methoxyphenol	0	0.115	0.115	0.003		
105	2,4-dimethylphenol	0.088	0.058	0.035	0.001		
106	3,5-dimethylphenol	0	0.112	0.044	0.002		
107	1,3-benzenediol	0	0	0	0.002		
108	4-methyl-2, 6-di-tert-butylphenol	0	0	0	0.001		
109	2,6-di-t-butyl-4-ethylphenol	0	0	0	0.001		
110	2,4,6-tri-t-butylphenol	0	0	0	0.001		
111	4-octylphenol	0	0.094	0.099	0.002		
112	2-chlorophenol	0	0.062	0.092	0.002	Intermediate of dyestuff and pesticide	
113	2,4-dichlorophenol	0	0.045	0.045	0.002	Int. of dyestuff	
114	2,6-dichlorophenol	0	0.012	0.014	0.001		
115	4-bromophenol	0	0	0	0.003		
116	4-chloro-3-methylphenol	0.012	0	0	0.003		
117	2,4,6-trichlorophenol	0	0.039	0.046	0.007	Int. of dyestuff fumgicide, wood preservatives	
118	2,4,5-trichlorophenol	0	0	0	0.009		
119	2,3,6-trichlorophenol	0.007	0	0	0.015		
120	2, 3, 4, 6-tetrachloro-phenol	0	0	0	0.001		
121	Pentachlorophenol	0	0	0	0.001		
122	Dimethyl phthalate	0	0.076	0.103	0.001	Plasticizer for celluloce acteate, perfume, material of insecticide	
123	Dimethylterephenol	0	1.16	0	0.001		
124	Diethyl phthalate	0	1.689	1.48	0.001	Plasticizer for celluloce acetate and poly styrene	

Table 1 (cont'd)

No.	VOC analyzed	Blank	Kuguri	Yotsutani	MDL, μg/L	Use and toxicity data	LC_{50}
125	Diisobutyl phthalate	0	0.051	0.044	0.001		
126	Di-*n*-butyl phthalate	0	0.839	0.859	0.001		
127	Butyl benzyl phthlate	0	0.058	0.075	0.005	Plasticizer of vinyl chloride	
128	Diheptyl phthalate	0	0.073	0.061	0.009		
129	Bis(2-ethylhexyl)-phthalate	0.006	1.111	1.576	0.006		
130	Di-*n*-octyl phthalate	0	0	0	0.17	Plasticizer of vinyl chloride	
131	Benzyl alcohol	0	1.575	2.646	0.003	Perfume for cosmetics of soap	
132	Alpha-terpineol	0	0.741	0.576	0.005		
133	Safrole	0	0	0	0.002	Disinfectant	
134	Isosafrole	0	0	0	0.002		
135	Dibenzofuran	0	0.005	0	0.001		
136	1,3-dichloro-2-propanol	0	0	0	0.002	Solvent for nitrocellulose, binder for water paint	
137	Aniline	0	0	0	0.001	Dye, rubber, medical, O. T. material for gunpowder	
138	N-methylaniline	0	0	0	0.001	Organic systhesis	
139	2-toluidine	0	0	0	0.001	Azo-dye, O.T.	
140	4-toluidine	0	0	0	0.002	O.T. solvent for dye synthesis	
141	3-toluidine		0	0	0.002		
142	N,N-dimethylaniline	0	0	0	0.001		
143	N-ethylaniline	0	0	0	0.001		
144	2,5-dimethylaniline	0	0	0	0.002		
145	2-anisidine	0	0	0	0.002	Int. of dye	
146	3,5-dimethylaniline	0	0	0	0.003		
147	2,3-xylidine	0	0	0	0.001		
148	3,4-xylidine	0	0	0	0.001		
149	4-anisidine	0	0	0	0.039	Int. of dye	
150	3-anisidine	0	0	0	0.008		
151	1-naphthylamine	0	0	0	0.01	Azo-dye, synthesis of acid	
152	2-naphthylamine	0	0	0	0.01		
153	diphenylamine	0	0.011	0.009	0.001	Material of rubber, dyestuff, stabilizer of powder	
154	Phenacetin	0	0	0	0.009		
155	N-phenyl-1-naphthylamine	0	0	0	0.003		
156	4-dimethylamino-azobenzene	0	0	0	0.004		
157	N-phenyl-2-naphthylamine	0	0	0	0.002		
158	2-chloroaniline	0	0.023	0	0.001	Int. of medical and pesticide	
159	3-chloroaniline	0	0	0	0.001		
160	4-chloroaniline	0	0	0	0.001	Manufucture inhibited	
161	5-chloro-2-methyl aniline	0	0	0	0.001		
162	2,4-dichloroaniline	0	0	0	0.002		
163	2,5-dichloroaniline	0	0.009	0	0.001	Int. of dye and pigments	
164	2,3-dichloroaniline	0.035	0	0.082	0.002		
165	2,4,6-trichloroaniline	0	0	0	0.002		
166	3,4-dichloroaniline	0	0	0	0.013	Int. of dye, material of pesticide	

Table 1 (cont'd)

No.	VOC analyzed	Blank	Kuguri	Yotsutani	MDL, μg/L	Use and toxicity data	LC_{50}
167	2-bromo-4,6-dichloroaniline	0	0	0	0.001		
168	4-bromo-2,6-dichloroaniline	0	0	0	0.001		
169	2,6-dibromo-4-chloroaniline	0	0	0	0.001		
170	2,4,6-tribromoaniline	0	0	0	0.001		
171	3,3'-dichloro-benzeidine	0	0	0	0.035		
172	4, 4'-methylene-bis-2-chloroaniline	0	0	0	0.012		
173	Quinoline	0	0.1	0.144	0.001		
174	Nitrobenzene	0	0	0	0.003		
175	2-nitrophenol	0	0	0	0.005		
176	2-nitrotoluene	0	0	0	0.001	Int. of dye	
177	3-nitrotoluene	0	0	0	0.002		
178	4-nitrotoluene	0	0	0	0.004		
179	3-nitroanisole	0	0	0	0.002		
180	4-nitroanisole	0.01	0	0	0.002		
181	2-nitroanisole	0	0	0	0.003		
182	2-nitroaniline	0.01	0	0	0.002		
183	2,6-dinitrotoluene	0	0	0	0.005		
184	3-nitroaniline	0	0	0	0.01		
185	2,4-dinitrotoluene	0.009	0	0	0.004		
186	3-nitroaniline	0	0	0	0.004		
187	2,4-dinitroaniline	0	0	0	0.003		
188	3-chloronitrobenzene	0	0	0	0.001		
189	3-dichloronitrobenzene	0.013	0	0	0.04		
190	4-chloro-2-nitroaniline	0	0	0	0.001		
191	2,6-dichloro-4-nitroaniline	0	0	0	0.007		
192	Pentachloroni-trobenzene	0	0	0	0.001		
193	N-nitrosodiethylamine	0	0	0	0.003		
194	N-nitrosopiperidine	0	0	0	0.002		
195	N-nitrosodi-n-butylamine	0.007	0	0	0.002		
196	Carbazole	0	0	0	0.001		
197	Dimethyl sulfone	0	0	0	0.2	Exist in nature	
198	Benzothiazol	0	0.378	0.081	0.001	Additive for rubber	
199	2-methylbenzothiazole	0	0	0	0.001		
200	2-(methylethio)-benzothiazole	0	0.138	0.133	0.001		
201	Dibenzothiophene	0	0	0	0.001		
202	Dipheneyldisulfide	0	0	0	0.001		
203	Phenothiazine	0.107	0	0	0.004		
204	Tributyl phosphate	0	0.015	0.018	0.008		
205	Dietyl-p-nitrophenyl phosphate	0	0	0	0.049		
206	Tris(2-ethylhexyl) phosphate	0	0	0	0.31		

Table 1 (cont'd)

No.	VOC analyzed	Blank	Kuguri	Yotsutani	MDL, μg/L	Use and toxicity data	LC_{50}
207	Tricrtesyl phosphate	0	0	0	0.006	Fireproof additive vinyl chloride resin, etc.	
208	Tris(2-chloroethyl) phosphate	0	0.1	0.177	0.003		
209	Tris(1,3-dichloro-2-propyl)phosphate	0	0	0	0.002	Pesticide (Insecticide)	
210	Fenobucarb	0	0.035	0.035	0.001	Pesticide (Insecticide)	16000 μg/L (Koi)
211	Alpha-HCH	0	0	0	0.001	Pesticide (Insecticide)	
212	Beta-HCH	0	0	0	0.001	Pesticide (Insecticide)	
213	Gamma-HCH	0.036	0	0	0.001	Pesticide (Insecticide)	
214	Diazinon	0	0	0	0.001	Pesticide (Insecticide)	2600—3200 μg/L
215	Delta-HCH	0	0	0	0.001	Pesticide (Insecticide)	
216	Heptachlor	0.014	0	0	0.001	Pesticide (Insecticide)	
217	Fenitrothion(MEP)	0.006	0	0	0.001	Pesticide (Insecticide)	
218	Chlorpyrifos	0	0	0	0.001	Pesticide (Insecticide)	3 μg/L (Nijimasu)
219	Aidrin	0	0	0	0.001	Pesticide (Insecticide)	
220	Isofenphos	0.01	0	0	0.005	Pesticide (Insecticide)	
221	Chlorfenvinphos	0	0	0	0.016	Pesticide (Insecticide)	
222	Heptachor epoxide	0	0	0	0.003	Pesticide (Insecticide)	
223	Trans-chlordane	0	0	0	0.001	Pesticide (Insecticide)	
224	Cis-chlordane	0	0	0	0.001	Pesticide (Insecticide)	
225	Endosulfan I	0	0	0	0.001	Pesticide (Insecticide)	
226	Trans-nonachlor	0	0	0	0.001	Pesticide (Insecticide)	
227	4,4'-DDE	0	0	0	0.001	Pesticide (Insecticide)	
228	Dieldrin	0	0	0	0.003	Pesticide (Insecticide)	
229	Isoxathion	0	0	0	0.023	Pesticide (Insecticide)	
230	Endrin	0	0	0	0.001	Pesticide (Insecticide)	
231	Endosulfan II	0	0	0	0.006	Pesticide (Insecticide)	
232	4,4'-DDD	0	0	0	0.001	Pesticide (Insecticide)	
233	Endrin alddehyde	0	0	0	0.008	Pesticide (Insecticide)	
234	Endosulfan sulfate	0	0	0	0.001	Pesticide (Insecticide)	
235	4,4'-DDT	0	0	0	0.002	Pesticide (Insecticide)	
236	Pyridaphenthion	0	0	0	0.048	Pesticide (Insecticide)	
237	Endrin ketone	0	0	0	0.001	Pesticide (Insecticide)	
238	EPN	0	0	0	0.025	Pesticide (Insecticide)	
239	Methoxychlor	0	0	0	0.002	Pesticide (Insecticide)	
240	Carbary (NAC)	0	0	0	0.001	Pesticide (Insecticide)	1950 μg/L (Nijimasu)
241	Dichlofenthion (ECP)	0	0	0	0.001	Pesticide (Insecticide)	
242	Buprofezin	0	0	0	0.001	Pesticide (Insecticide)	
243	Malathion	0	0	0	0.001	Pesticide (Insecticide)	
244	Chlorpyriphos oxon	0	0	0	0 001	Pesticide (Insecticide)	
245	Isofenphos oxon	0	0	0	0.001	Pesticide (Insecticide)	
246	Benfluralin	0	0	0	0.001	Pesticide (Herbicide)	
247	Simazine (CAT)	0	0	0	0.01	Pesticide (Herbicide)	

Table 1 (cont'd)

No.	VOC analyzed	Blank	Kuguri	Yotsutani	MDL, μg/L	Use and toxicity data	LC_{50}
248	Propyzamide	0	0	0	0.005	Pesticide (Herbicide)	
249	Terbucarb (MBPMC)	0	0	0	0.001	Pesticide (Herbicide)	
250	Thiobencarb	0	0	0	0.002	Pesticide (Herbicide)	
251	Pendimethalin	0	0	0	0.001	Pesticide (Herbicide)	
252	Methyl dymron	0	0	0	0.004	Pesticide (Herbicide)	
253	Butamifos	0	0	0	0.001	Pesticide (Herbicide)	
254	Napropamide	0	0	0	0.005	Pesticide (Herbicide)	
255	CNP amino type	0	0	0	0.001	Pesticide (Herbicide)	
256	Nitrofen(NIP)	0	0	0	0.016	Pesticide (Herbicide)	
257	Chlornitrrofen (CNP)	0	0	0	0.001	Pesticide (Herbicide)	
258	Chlomethoxyfen (X-52)	0	0	0	0.2	Pesticide (Herbicide)	
259	Esprocarb	0	0	0	0.001	Pesticide (Herbicide)	
260	Simetryn	0	0.035	0.026	0.001	Pesticide (Herbicide)	7000 μg/L (Masu 96h)
261	Bromobutide	0	0	0	0.001	Pesticide (Herbicide)	
262	Mefenacet	0	0	0	0.001	Pesticide (Herbicide)	
263	Molinate	0	0	0	0.001	Pesticide (Herbicide)	
264	Pretilachlor	0	0	0	0.001	Pesticide (Herbicide)	
265	Butamifos oxon	0	0	0	0.001	Pesticide (Herbicide)	
266	Etridiazole-(Echlomezol)	0	0	0	0.004	Pesticide (Fungicide)	
267	Chloroneb	0	0	0	0.001	Pesticide (Fungcide)	
268	Pencycuron	0	0	0	0.006	Pesticide (Fungicide)	
269	Chlorothalonil (TPN)	0	0	0	0.002	Pesticide (Fungicide)	
270	Iprobenfos (IBP, Kitazin P)	0	0	0	0.023	Pesticide (Fungicide)	
271	Tolclofos-methyl	0	0	0	0.002	Pesticide (Fungicide)	
272	Captan	0	0	0	0.007	Pesticide (Fungicide)	
273	Flutolanil	0	0	0	0.004	Pesticide (Fungicide)	
274	Isoprothiolane	0	0	0	0.008	Pesticide (Fungicide)	
275	Iprodione	0	0	0	0.001	Pesticide (Fungicide)	
276	Mepronil	0	0	0	0.01	Pesticide (Fungicide)	
277	Edifenphos (EDDP)	0	0	0	0.001	Pesticide (Fungicide)	
278	Tricyclazole	0	0	0	0.001	Pesticide (Fungicide)	
279	Fthalide	0	0	0	0.001	Pesticide (Fungicide)	
280	Probenazole	0	0	0	0.001	Pesticide (Fungicide)	
281	Diisopropyl chloromalenate	0	0	0	0.001		
282	Diisopropyl dichloromalenate	0	0	0	0.001		
283	Tololophos-methyl oxon	0	0	0	0.001	Pesticide (Fungicide)	

In Table 2, COD levels for both samples were significantly higher than the quality standards for rivers in Kitakyushu area. The increasing concentrations of COD in both samples indicates possible discharge of domestic waste from certain fugitive sources (non-point) into the specified sampling sites, consequently resulting to organic matter enrichment in the water body. Total concentrations of lead (Pb = 0.072 mg/L; 0.093 mg/L) and dissolved and total concentrations of cadmium (Cd = 0.004/0.009 mg/L; 0.011/0.018 mg/L) in both samples were invariably higher than the maximum standard limits (Pb = 0.005 mg/L, Cd = 0.001 mg/L, respectively) for human

health hazards. Since, Pb has no known functions or health benefits for human or other living organisms, in Table 3, the LC_{50} level of 0.14 mg/L in rainbow trout (hypercritical species) ascertain the potential dangers of this heavy metal in the food chain. Therefore, regular routine monitoring on seasonal basis could be a recommended approach for proper verification. From Yotsutani sample, zinc (Zn) concentrations (soluble = 5.2 mg/L, total = 6.2 mg/L) slightly exceeded that of industrial wastewater maximum standard level (5 mg/L) for Kitakyushu area. Concentrations of cyanide (CN), chromium (Cr^{6+}) (carcinogenic substances) and Cu were however, not detected in the respective samples.

Table 2 Results of average concentrations of contaminants detected in water samples in comparison with water quality standards for Kitakyushu City

Average concentrations: mg/L

Parameter			Kuguri sample	Yotsutani sample	Maximum standards
COD			10	11	5
CN			N.D.	N.D.	0.1
Cr^{6+}			N.D.	N.D.	0.005
Heavy metals	Pb	Soluble	N.D.	N.D.	
		Total	0.072	0.093	0.005
	Cd	Soluble*	0.004	0.011	0.001
		Total	0.009	0.018	
	Cu	Soluble*	N.D.	N.D.	0.03
		Total	N.D.	N.D.	
	Zn	Soluble**	3.2	5.2	0.5
		Total	3.4	6.2	
S-VOC			See Table 1		

* samples filtered with 1.0 μm pore sizes; * * samples filtered with 0.45μm pore sizes

Results in Table 3 specifically showed pertinent parameter estimation for Pb, Cd, Cu, Zn, phenol and 3-,4-cresols as potential contaminants in the samples with respect to LC_{50} test. Based on this statistical evaluation, Cd and Zn levels showed significantly higher toxicity levels above the LC_{50} limits of survival in specific period of time, especially for hypercritical fish species such as rainbow trout and carp fish. Under this sort of polluted condition, fish species whose characteristics are very similar to these very less tolerance species to toxicity would eventually be faced with difficulty of survival. The phenol and 3-, 4-cresols also indicated relatively higher toxicity levels in both samples.

Table 3 Toxicity test for potential risk hazards in fish Average concentration: mg/L

Pollutant class	Parameter	Detected value soluble/total		Toxicity level, LC_{50}
		Kuguri	Yotsutani	
Heavy metals	Pb	<0.005/0.072	<0.005/0.093	0.14 (rainbow trout, 96h)
	Cd	0.004/0.009	0.011/0.018	0.007 (rainbow trout, 96h)
	Cu	<0.03/0.03	<0.03/<0.03	0.02 (rainbow trout, 96h)
				0.75(rainbow trout, 48h)
	Zn	3.2/3.4	5.2/6.2	0.41—0.72 (rainbow trout, 96h)
				20 (koi, 24h)
				3.3 (oikawa, 24h)
Organic compounds	Phenol	0.0037	0.0043	15 (koi, 168h)
				4 (rainbow treut, 18h)
	3-cresol	0.0069	0.0056	25 (crucian carp, 24h)
	4-cresol			21 (crucian carp, 24h)

However, it may be contentious to reach a conclusion by this investigation that the verified TL_{50} test can substantiate adequate evaluation of any potential hazard in the aquatic environment with only three consecutive routine monitoring data. Therefore, periodic inspection for a considerable time of one year is capable of providing a more reliable and identifiable ability of this highly sensitive analytical method.

5 Conclusion

Experimental analysis confirmed that there were high concentrations of Zn and Cd in the samples above the maximum standard levels for rivers in Kitakyushu area. And for certain hypercritical fish (rainbow trout, oikawa, koi, crucian carp fish etc.), even an insignificant toxicity from most of these substances in water may cause considerable undesirable impact with eventual fish kill. This reason however, is not sufficient enough to clearly justify the incidence of fish kills at the sampling point due to the fact that other limiting factors were not thoroughly investigated. It is also very difficult to draw up any conclusion about the fact of organic compounds discovered in the samples, since the data in question for the respective parameters (phenol, 3-cresol and 4-cresol) were obtained from only three sampling periods for each sampling point. COD concentrations in both samples however showed intrinsic values indicative of the possibility of domestic wastewater discharge into the river.

In an effort to substantiate the consequences of pollution impact, especially for VOC in an aquatic environment, further investigation would be required considering other limiting factors in a form of routine monitoring on both the water samples and fish for a longer period of time, preferably one year. Nevertheless, the results obtained from the analysis could serve as a benchmark through which other phenomena can easily be investigated, and the GC－Ion Trap for simultaneous analysis of over 200 VOC is not only advanced with high precision quality, but widely employed in analytical chemistry.

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