

Appendix D

Summary of Analytical Method in Environmental Survey

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Substances subject to environmental survey for water system

Name of Substances	Analytical Method / Flow Sheet	Remarks
① (1)Dibutyltin comp'ds (2)Phenyltin comp'ds (3)Diphenyltin comp'ds	<p>Water</p> <pre> graph LR A[Sample 1L NaCl 30g, pH5] --> B[Derivatization NaBEt4] B --> C[Extraction Hexane 100,50ml] C --> D[Dehydration/ Concentration 0.2ml] D --> E[GC/MS-SIM] </pre> <p>Bottom Sediments</p> <pre> graph LR A[Sample 2g Surrogate substances] --> B[Extraction 1M HCl-MeOH /AcEt(1:1) 20ml, 20ml] B --> C[Derivatization pH5 NaBEt4] C --> D[Extraction Hexane 5ml, 5ml] D --> E[Dehydration/ Concentration ca. 1ml] E --> F[Clean-up Flosil Column Cartridge] F --> G[Concentration 0.2ml] G --> H[GC/MS-SIM] </pre> <p style="text-align: right;">(Developed by Kitakyusyu City)</p>	<p>GC/MS-SIM</p> <p>Column: DB-5ms Column length: 30m Column I.D.: 0.25mm Film thickness: 0.25 μ m</p> <p>Detection limit</p> <p>Water: μ g/l</p> <p>(1) 0.00042 (2) 0.0055 (3) 0.00025</p> <p>Bottom sediments: μ g/g</p> <p>(1) 0.0014 (2) 0.016 (3) 0.00017</p>
② (4)Aniline (5)4-Ethoxyaniline (6)o-Chloroaniline (7)m-Chloroaniline (8)p-Chloroaniline (9)2,4-Dichloroaniline (10)2,5-Dichloroaniline (11)3,4-Dichloroaniline (12)o-Toluidine (13)m-Toluidine (14)p-Toluidine	<p>Water</p> <pre> graph LR A[Sample 500ml Surrogate Aniline-d5 100ppm, 10 μ l] --> B[Solid Phase Extraction Sep-Pak Plus PS-2] B --> C[Elute AcMt 3ml] C --> D[Concentration N4 ~1ml] D --> E[Add Internal St'd Naphthalene-d8 Acenaphthene-d10 Phenanthrene-d10 1ppm each/Hex 1ml] E --> F[Dehydration anhydrous Na2SO4 3g] F --> G[GC/MS-SIM] </pre> <p>Bottom sediments</p> <pre> graph LR A[Sample 20g Surrogate Aniline-d5 100ppm, 10 μ l] --> B[Steam distillation Sampling 500ml] B --> C[continue on *] </pre> <p style="text-align: right;">(Developed by Osaka Pref.)</p>	<p>GC/MS-SIM</p> <p>Column: HP-20M Column length: 25m Column I.D.: 0.2mm Film thickness: 0.2 μ m</p> <p>Detection limit</p> <p>Water: μ g/l</p> <p>(4) 0.059 (5) 0.249 (6) 0.088 (7) 0.107 (8) 0.066 (9) 0.067 (10) 0.062 (11) 0.084 (12) 0.061 (13) 0.145 (14) 0.081</p> <p>Bottom sediments: μ g/g</p> <p>(4) - (5) 5.3 (6) 4.5 (7) 4.4 (8) 4.6 (9) 3.5 (10) 1.9 (11) 5.0 (12) 2.0 (13) 3.7 (14) 3.0</p>

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③ (15)Acrylamide	<p>Water</p> <p style="text-align: center;">*</p> <pre> graph LR A[Sample 500ml] --> B[Filtration Glass filter] B --> C[Solid state extraction Sep-pak AC-2 (Precolumn: Sep-Pak C18)] C --> D[Elute Methanol 5ml] D --> E[Derivatizat'n 10%Xanthidrol /MeOH Soln: 100 μ l] E --> F[Solvent extract'on Dichloromethane 20ml, 20ml] F --> G[Dehydrat'n anhydrous Na2SO4] G --> H[Concentrat'n Rotary evapo- rater(<35°C)] H --> I[Const. Volume 1ml (add internal Stand'd)] I --> J[GC/MS-SIM] </pre> <p>Bottom sediments</p> <pre> graph LR K[Sample 20g] --> L[Water extract'n Pure water: 150ml (Ultrasonic extract'n 15min)] L --> M[Centrifuge 2,500rpm 10min] M --> N[continue on *] </pre> <p style="text-align: right;">(Developed by Aichi Pref.)</p>	<p>GC/MS-SIM</p> <p>Column: DB-5ms Column length: 30m Column I.D.: 0.25mm Film thickness: 0.25 μ m</p> <p>Detection limit Water: 0.12 μ g/l Bottom sediments: 4.0 μ g/kg</p>
④ (16)Pyridine	<p>Water</p> <p style="text-align: center;">*</p> <pre> graph LR O[Sample 500ml Pyridine-d5] --> P[Solid Phase Extraction Bond Elut C8, AC-2] P --> Q[Elute Acetone Dichloro- methane 5ml Backflush] Q --> R[Dehydration anhydrous Na2SO4] R --> S[Concentration 1ml N2, <35°C] S --> T[GC/MS-SIM] </pre> <p>Bottom sediments</p> <pre> graph LR U[Sample 20g Pyridine-d5] --> V[Extraction Pure water 50ml x 2 Shaking 10min Ultrasonic 10min] V --> W[Centrifuge 2,800rpm 10min] W --> X[continue on *] </pre> <p style="text-align: right;">(Developed by Nagano Pref.)</p>	<p>GC-MS</p> <p>Column: HP INOWAX Column length: 30m Column I.D.: 0.32mm Film thickness: 0.5 μ m</p> <p>Detection limit Water: 90ng/l Bottom sediments: 4.5 ng/g</p>

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⑤ (17)N,N-Dimethyl- formamide	<p>Water</p> <pre> graph LR S1[Sample 500ml] --> A1[Add DMF-d7 1 μg] A1 --> E1[Solid state extraction AC-2 Cartridge] E1 --> EL1[Elute Methanol 3ml] EL1 --> C1[Concentrat'n] C1 --> D1[Dehydrat'n Anhydrous Na2SO4] D1 --> C2[Concentrat'n] C2 --> GC1[GC/MS] Ethyl acetate --> D1 </pre> <p>Bottom sediments</p> <pre> graph LR S2[Sample 20g] --> A2[Add DMF-d7] A2 --> U[Ultrasonic extract'n Pure water: 30ml 15min] U --> C[Centrifuge 2,500rpm 5 min] C --> GC2[GC/MS] U --- R[repeat 3 times] </pre> <p>continue on *</p> <p style="text-align: right;">(Developed by Niigata Pref.)</p>	<p>GC/MS-SIM Column: DB-WAX Column length: 30m Column I.D. : 0.25mm Film thickness: 0.5 μ m</p> <p>Detection limit Water: 0.065 μ g/l Bottom sediments: 1.89 μ g/kg</p>
⑥ (18)N-t-Butyl-2-benzo- thiazolsulfenamide (19)N-Cyclohexyl-2- benzothiazol- sulfenamide (20)N,N-Dicyclohexyl- 2-benzothiazol- sulfenamide	<p>Water</p> <pre> graph LR S3[Sample 1L] --> E3[Extraction Hexane 50ml × 2] E3 --> C3[Concentrat'n] C3 --> GC3[GC/MS-SIM] </pre> <p>Bottom sediments</p> <pre> graph LR S4[Sample 10g] --> E4_1[Extract'n Acetone 50ml × 2] E4_1 --> E4_2[Extract'n Pure water 500ml Hexane 50ml × 2] E4_2 --> C4[Concentrat'n] C4 --> GC4[GC/MS-SIM] </pre> <pre> graph LR S5[Sample 10g] --> P[Hexane/Acetonitril Partition] P --> E5_1[Extract'n Pure water 500ml Hexane 50ml × 2] E5_1 --> C5[Concentrat'n] C5 --> GC5[GC/MS-SIM] </pre> <pre> graph LR S6[Sample 10g] --> C6[Concentration] C6 --> GC6[GC/MS-SIM] </pre> <p>5%Hydrated silica gel chromatography purge 1%Acetone-Hexane 0-55ml collect 1%Acetone-Hexane 55-95ml</p> <p style="text-align: right;">(Developed by Tokyo Metro.)</p>	<p>GC/MS-SIM Column: DB-1 Column length: 30m Column I.D.: 0.25mm Film thickness: 0.1 μ m</p> <p>Detection limit Water: μ g/l (18) 0.086 (19) 0.21 (20) 0.26</p> <p>Bottom sediments: μ g/kg (18) 2.31 (19) 4.97 (20) 3.20</p>

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⑦ (20)Benzothiophene (21)Dibenzothiophene	<p>Water</p> <pre> graph LR A[Sample 1L NaCl 30g (no sea water)] --> B[Solvent Extract'n Acetone 50ml Hexane 100, 50ml] B --> C[Dehydrat'n Concentrat'n anhydrous Na2SO4] C --> D[Sep Pak Plus Silica gel 1%Acetone- Hexane 10ml] D --> E[Concentrat'n] E --> F[GC/MS] </pre> <p>Bottom sediments / Wildlife</p> <pre> graph LR A[Sample 20g] --> B[Alkali decomposit'n 1N KOH/EtOH 50ml Heating/reflux (Bottom 1hr) Room temp. decomp.(Wildlife 15hr)] B --> C[Standing to cool Hexane 50ml] C --> D[Extraction Hexane:Ethanol(1:1)20ml Pure water :50ml after Ex. Hexane 50ml re-Ex] D --> E[Washing Pure water 50, 25ml] E --> F[Dehydrat'n/Concentrat'n] F --> G[Column chromatography 5%Hydrated Silica gel (5g,10mm φ) 1st Hexane 15ml 2nd 1%Acetone-Hexane 100ml] G --> H[Concentrat'n] H --> I[GC/MS] </pre> <p>(Developed by Okayama Pref.)</p>	<p>GC-MS Column: Quadrex MS Column length: 25m Column I.D. : 0.25mm Film thickness: 0.25 μ m</p> <p>Column: DB-5MS Column length: 30m Column I.D.: 0.25mm Film thickness: 0.25 μ m</p> <p>Detection limit water: μ g/l (21) 0.040 (22) 0.01640</p> <p>bottom sediments: μ g/kg (21) 1.9 (22) 2.1</p> <p>fishes: μ g/kg (21) 0.61 (22) 0.34</p>
⑧ (23)Nonionic surfac- tants	<p>Water</p> <pre> graph LR A[Sample 1L NaCl 100g (No sea water)] --> B[Solvent Extract'n /Dehydrat'n EtAc 120, 100ml Anhydrous Na2SO4] B --> C[Concentrat'n /Solution Water:MeOH(1:1) 10ml] C --> D[Cleanup Sep Pak CM-QMA-C18 1)Washing:MeOH 20ml 2)Add sample, adsorb on C18 3)Elut'n: MeOH 4ml] D --> E[React'n w. HBr 1)Evaporat'n to dryness 2)HBr:MeOH(1:1) 0.5ml 3)2hr reaction at 150°C in hard ampoule] E --> F[Solvent Extract'n Hexane 1 to 10ml] F --> G[GC/MS] H[Internal Standard(p-Xylene d10)] --> G </pre> <p>Bottom sediments</p> <pre> graph LR A[Sample 20g] --> B[MeOH Extract'n MeOH 40ml×2 Centrifuge (3,000rpm, 5min)] B --> C[Hexane wash n-Hexane 30ml×2 Pure water 70ml add] C --> D[Filtrat'n GF/F] D --> E[continue on *] </pre> <p>(Developed by Okayama Pref.)</p>	<p>GC-MS Column: VOCOL Column length: 60m Column I.D.: 0.75mm Film thickness: 1.5 μ m</p> <p>Detection limit Water: 2.5 μ g/l Bottom sediments: 38 μ g/kg</p>

Name of Substances	Analytical Method / Flow Sheet	Remarks
⑨ (24)Phenol	<p>Water</p> <p style="text-align: center;">*</p> <pre> graph LR A[Sample 1L Add surrogate NaCl (15g)] --> B[Adjust to pH3 6M HCl] B --> C[Extraction Dichloromethane 100ml x 2] C --> D[Dehydrat'n/Concentrat'n/Transfer to solvent 2-Propanol (1ml)] D --> E[Derivatizat'n PFBB Sol'n(2ml) K2CO3, 3mg 80°C, 30min] E --> F[Water wash Hexane(10ml) Pure water(30ml)] F --> G[Concentrat'n] G --> H[Cleanup Omission allowed for hindering materials exist less] H --> I[GC/MS-SIM Phenanthrene-d10] </pre> <p>Bottom sediments</p> <pre> graph LR J[Sample 10g Add surrogate] --> K[Extraction 0.1M NaOH/MeOH (30ml) x 2] K --> L[Washing Pure water(500ml) Dichloromethane(50ml)] L --> M[Continue on * , after adding 15g NaCl] </pre> <p>Wildlife</p> <pre> graph LR N[Sample 2g Add surrogate] --> O[Extraction MeOH(50ml) x 2] O --> P[MeOH/Hexane Partition Pure water(3ml) Hexane(10ml) x 2] P --> Q[Dilution 3%NaCl Sol'n(500ml)] Q --> R[Continue on *] </pre> <p style="text-align: right;">(Developed by Kita- Kyushu City)</p>	<p>GC-MS-SIM</p> <p>Column: DB-1701</p> <p>Column length: 30m</p> <p>Column I.D. : 0.25mm</p> <p>Film thickness: 0.25 μ m</p> <p>Detection limit</p> <p>Water:</p> <p style="padding-left: 20px;">0.028 ng/ml</p> <p>Bottom sediments:</p> <p style="padding-left: 20px;">0.00535 μ g/g</p> <p>Wildlife:</p> <p style="padding-left: 20px;">0.0187 μ g/g</p>

Name of Substances	Analytical Method / Flow Sheet	Remarks
③ (21-1)1-Methyl-naphthalene (21-2)2-Methyl-naphthalene (22-1)1,2-Dimethyl-naphthalene (22-2)1,3+1,6-Dimethylnaphthalene (22-3)1,4-Dimethyl-naphthalene (22-4)1,5-Dimethyl-naphthalene (22-5)1,7-Dimethyl-naphthalene (22-6)1,8-Dimethyl-naphthalene (22-7)2,3-Dimethyl-benzene (22-8)2,6-Dimethyl-naphthalene (22-9)2,7-Dimethyl-naphthalene	<pre> graph LR A[Air Sample 40L] --> B[Adsorption Collection Tenax TA 50mg] B --> C[H2SO4 washing TCT] C --> D[GC-MS-SIM] </pre> <p style="text-align: right;">(Developed by Kawasaki City)</p>	GC/MS-SIM Column: SPB-50 Column length: 30m Column I.D.: 0.32mm Film thickness: 0.25 μ m Detection limit: μ g/m ³ (21-1) 0.15 (21-2) 0.41 (22-1) 0.10 (22-2) 0.15 (22-3) 0.10 (22-4) 0.08 (22-5) 0.10 (22-6) 0.08 (22-7) 0.10 (22-8) 0.13 (22-9) 0.12
④ (23)Crotonaldehyde	<pre> graph LR A[DNHPSilica Cartridge Collection Ozone scrubber, 2 in parallel, warmed] --> B[Solvent Removal TOYOPAK IC-SP Acetonitrile] B --> C[Evaporation to dryness RE] C --> D[Re-dissolut'n EtAC 100 μg/l 0.1 ppm Decanonitrile] D --> E[GC/MS] </pre> <p style="text-align: right;">(Developed by Osaka City)</p>	GC-MS Column: DB-5 Column length: 30m Column I.D.: 0.32mm Film thickness: 0.25 μ m Detection limit 0.004 μ g/m ³