

1 **Simple mercury determination using enclosed quartz cell with cold vapour-atomic absorption**  
2 **spectrometry**

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## 18 Experimental

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### 20 Instruments

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22 For mercury (Hg) monitoring, an atomic absorption spectrometric (AAS) system (AAAnalyst 200,  
23 PerkinElmer Co. Ltd., USA) was used, the analytical conditions for which are summarised in Table  
24 S1. As a typical Hg vaporisation method, the AAS system was equipped with a Hg hydride system  
25 (MHS-15, PerkinElmer Co. Ltd., USA); the set vaporisation conditions of the system are  
26 summarised in Table S2. The AAS system was further equipped with a standard quartz cell (12.5 ×  
27 12.5 × 58 mm) with a screw cap and rubber septum (S15-UV-10, GL Sciences Inc., USA), assisted  
28 by a polylactic resin cell guide printed using a three-dimensional printer (da Vinci mini Maker 3D  
29 Printer, Taiwan) as shown in Fig. 1.

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31 Table S1 Analytical conditions of the AAS.

AAS system	AAAnalyst200
Operating principle	Double beam system
Lamp	Electrodeless Discharge Lamp (EDL) system II
Lamp current	220 mA
Wavelength	253.7 nm
Measurement mode	peak height
Slit width	2.7/2.3 nm

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35 Table S2 Comparison between the developed and conventional CV methods for the reduction of Hg.

CV system	Mercury Hydride system (MHS)-15	Enclosed Quartz Cell (EQC)
Quartz cell shape	T shape quartz cell	Screw-cap quartz cell cuvettes
Light pass length	122 mm	10 mm
Inert carrier gas	Nitrogen gas	Not required
Nitrogen carrier gas pressure	260 kPa	–
Nitrogen gas consumption	1100 mL/min	–
Sample volume	10-20 mL	400 µL
Reductant volume	2.0 mL	40 µL

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### 38 Reagents

39 Reagents including SnCl<sub>2</sub>·H<sub>2</sub>O, KMnO<sub>4</sub>, KOH, 60 w/w% HNO<sub>3</sub>, 35 w/w% HCl, and 100 w/w%  
40 CH<sub>3</sub>COOH were purchased from FUJIFILM Wako Pure Chemical Corp. (Osaka, Japan) Ultra-pure

41 water ( $> 18.2 \text{ M}\Omega\text{cm}$ , PURELAB flex 3, ELGA-Veolia, High Wycombe, UK) was used for the  
42 preparation of standard, reductant, extracting, and other stock solutions.

43 Certified reference materials for Hg in soils (JSAC 0463) were purchased from the Japan Society for  
44 Analytical Chemistry (JSAC).

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#### 46 Sequential extraction procedure

47 In this study, Hg was extracted using a sequential extraction procedure reported by Bloom et al.<sup>1</sup>, as  
48 follows. Fraction 1 (attributed to water-soluble Hg): deionised water (25 mL) was added to the soil  
49 sample (certified reference materials for Hg in soils: JSAC 0463, 0.25 g), followed by  $18 \pm 4 \text{ h}$  of  
50 shaking at 1500 rpm. After extraction, the samples were centrifuged (3000 rpm) for 1 h, and filtered  
51 using a hydrophilic polytetrafluoroethylene syringe filter with a pore size of  $0.45 \mu\text{m}$  (DISMIC®-  
52 25HP, Advantec Toyo Kaisha, Ltd., Tokyo, Japan), followed by oxidation with  $\text{KMnO}_4$  (5 w/w%,  
53 25  $\mu\text{L}$ ). Fraction 2 (attributed to human-stomach-acid-soluble Hg): mixed acid (0.1 M  $\text{CH}_3\text{COOH}$   
54 and 0.01 M  $\text{HCl}$ , 25 mL) was added to the residue of the previous extraction and was shaken for  $18$   
55  $\pm 4 \text{ h}$  at 1500 rpm. The solution was then processed as per Fraction 1. Fraction 3 (attributed to  
56 organo-complexed Hg):  $\text{KOH}$  (1 M, 25 mL) was added to the residue of Fraction 2, then was shaken  
57 for  $18 \pm 4 \text{ h}$  at 1500 rpm. The solution was then processed as per Fraction 1 except that  $\text{HNO}_3$  (60  
58 w/w%, 2.5 mL) was added owing to the high neutralising capacity of the  $\text{KOH}$ . Fraction 4  
59 (attributed to elemental Hg or strongly complexed Hg):  $\text{HNO}_3$  (60 w/w%, 25 mL) was added to the  
60 residue of Fraction 3, then was shaken for  $18 \pm 4 \text{ h}$  at 1500 rpm. The solution was then processed as  
61 per Fraction 1, except that filtration was not performed. Fraction 5 (attributed to  $\text{HgS}$ ): the residue  
62 from Fraction 4 was digested with aqua regia at room temperature,  $22 \text{ }^\circ\text{C}$ .

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#### 64 Notes and references

65 1 N. S. Bloom, E. Preus, J. Katon and M. Hiltner, *Anal. Chim. Acta*, 2003, 479, 233.

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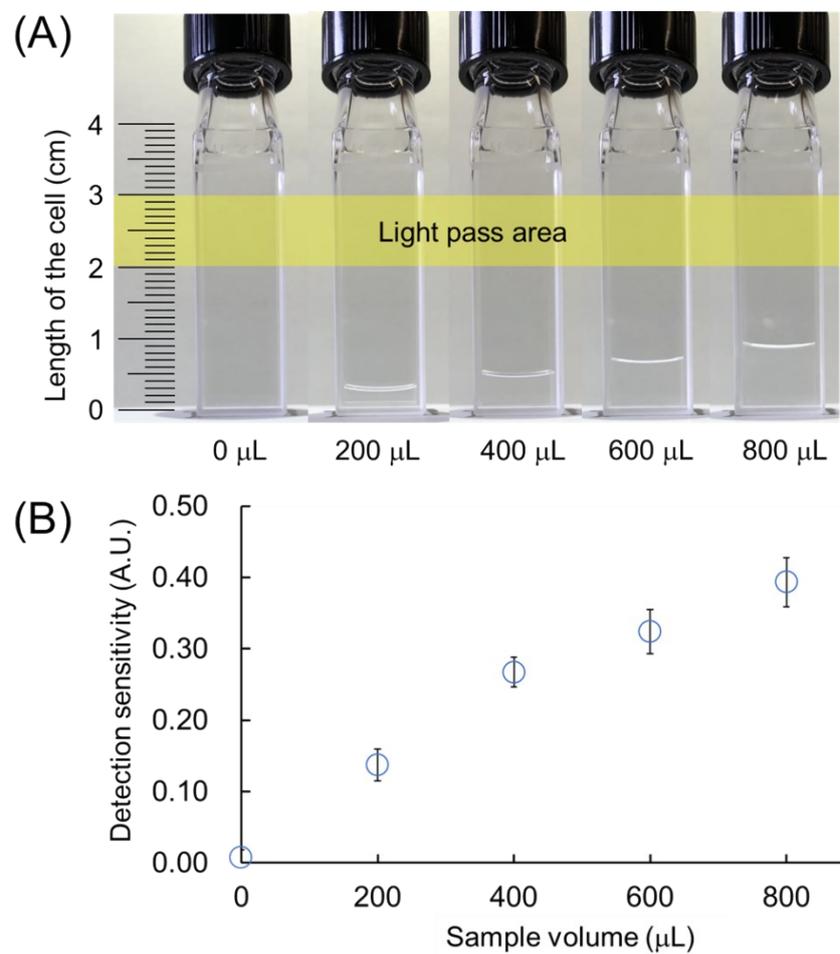
67 Table S3 Analytical performance comparison of the developed EQC- and conventional CV-AAS.

Analytical performances	Conventional method (CV-AAS)	Developed method (EQC-CV-AAS)
Linearity range, µg/L	0.50-50	0.50-100
Correlation coefficient, $R^2$	0.9990	0.9992
RSD, % (n = 5, 10 µg/L Hg)	3.65	4.10
RSD, % (n = 5, 50 µg/L Hg)	0.720	0.600
LOD, µg/L (S/N = 3.3)	0.0360	0.442
LOQ, µg/L (S/N = 10)	0.118	1.46

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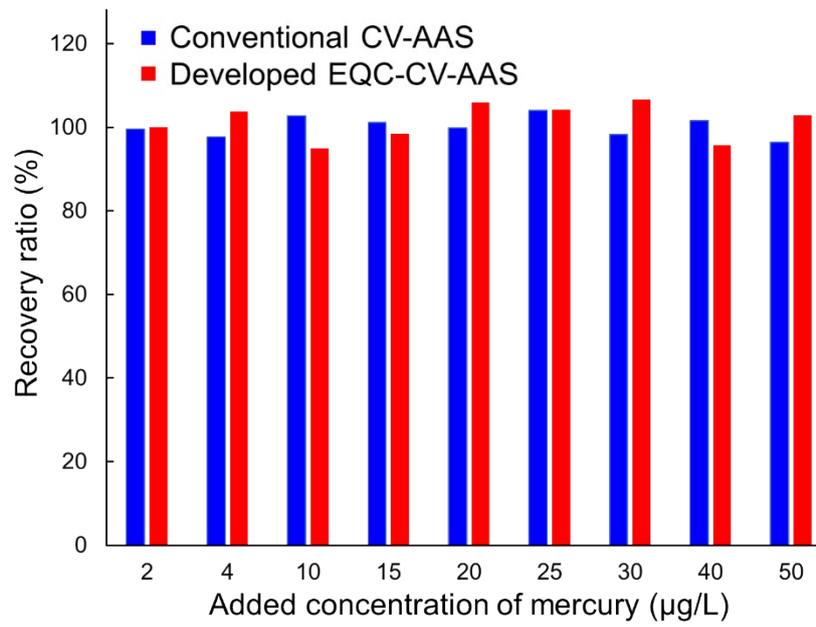
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72 Fig. S1 Changes in the liquid level (A) and detector responses (B) by increasing the sample volume.

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77 Fig. S2 Analysis of the river water sample with the artificially added Hg standard (2–50 µg/L).

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