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Supplemental Material

Removal of iodide from water by chlorination and subsequent adsorption on powdered activated carbon

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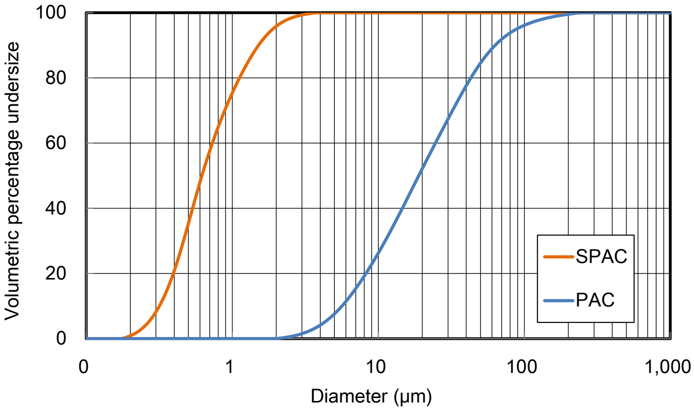

Figure S1. Particle diameter distributions of PAC and SPAC.

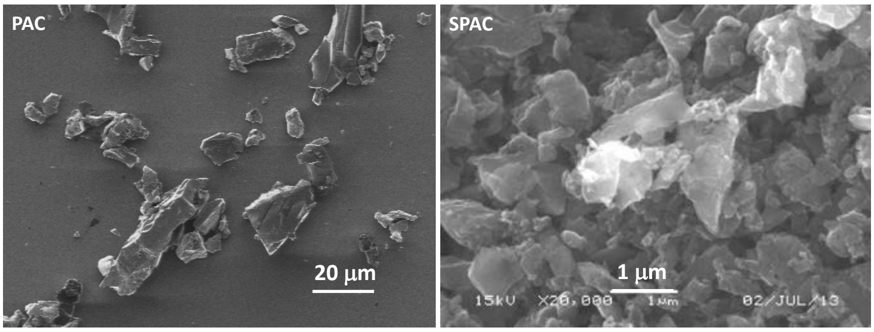

Figure S2. Scanning electron microscopy images of PAC (left) and SPAC (right).

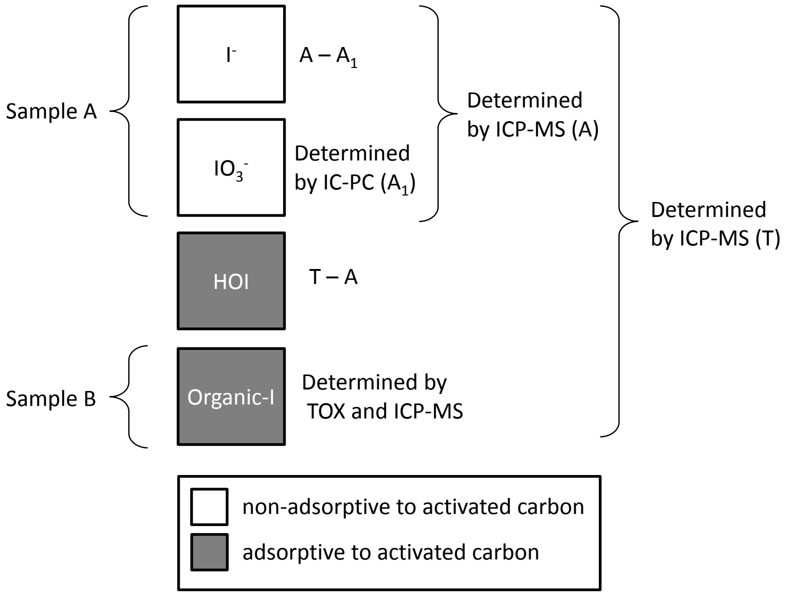

Figure S3. Image of iodine fractionation method

Section 1: Preliminary adsorption experiment

The effects of carbon dose and SPAC and PAC particle sizes are shown in Figure S3. Samples were chlorinated prior to treatment with PAC/SPAC. PAC at a dose of 20 mg/L removed about 20% of the iodine after a contact time of 30 min, whereas SPAC at the same dose removed 60% of the iodine. The residual iodine ratios decreased with increasing SPAC dose: after a contact time of 30 min, the removal percentages were 11%, 60%, and 85% at doses of 1, 20, and 100 mg/L, respectively. Moreover, at a SPAC dose of 100 mg/L, the equilibrium removal percentage was attained after a contact time of only 1 min. However, increasing the carbon dose from 100 to 200 mg/L did not result in any further enhancement of iodine removal, which indicates that the iodine remaining after 30 min at the 100 mg/L dose was in the form of species that were not adsorbed by carbon (that is, I^- and IO_3^-).

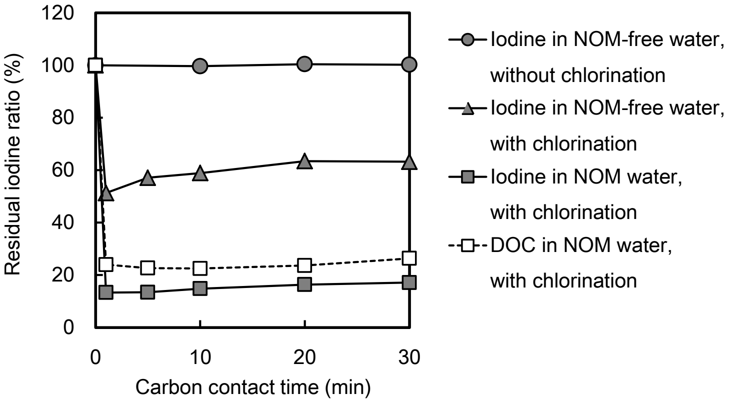

Figure S4. Changes in residual iodine ratio with carbon contact time. Initial I^- concentration in sample water, 10 μg-I/L; initial DOC concentration, 1.5 mg-C/L; chlorine dose, 1 mg-Cl_2/L; chlorination time, 10 min.

Section 2: TOX analysis

The organic-I concentrations were measured by means of TOX analysis, as follows. After chlorination for 6.5 min, 40 mL of NOM water was applied to a column of activated carbon (TOX-100, Mitsubishi Chemical Analytech, Kanagawa, Japan). It took 7 min for the 40-mL volume of the sample to pass through the column. Therefore, the chlorination time ranged from 6.5 to 13.5 min; the average chlorination time was 10 min. Then the column was washed with 10 mL of KNO_3 solution (0.08 M) to remove any HOI bound to the column. The carbon packing was then removed from the column and heated in a muffle furnace at 800 °C for 10 min, and the combustion gas was bubbled through 10 mL of Milli-Q water (the resulting solution was designated as Sample B). Any iodine in Sample B was regarded as organic-I (Tate et al. 1986). The iodine concentration in Sample B was determined by means of ICP-MS.

Section 3: Alternate method of iodine fractionation

After chlorination for 6.5 min, 40 mL of sample water was applied to an activated carbon column (TOX-100, Mitsubishi Chemical Analytech Co., Kanagawa, Japan). It took 7 min to pass the 40-mL volume of the sample through the column, and therefore the chlorination time ranged from 6.5 to 13.5 (=6.5+7) min and the average chlorination time was 10 min. The collected eluent was designated as Sample C; the average oxidation time was 10 min. The iodine in Sample C consisted of I^- and IO_3^- (Watanabe et al. 2011). Then the column was washed with 10 mL of KNO_3 solution (0.08 M) to remove adsorbed HOI, and the collected eluent was designated as Sample D. The carbon packing was removed from the column and heated in a muffle furnace at 800 °C for 10 min, and the combustion gas was bubbled through 10 mL of Milli-Q water (the resulting solution was designated as Sample E). The iodine in Sample E was regarded as organic-I (Tate et al. 1986). The iodine concentrations in Samples C, D, and E were determined by inductively coupled plasma mass spectrometry (ICP-MS). The IO_3^- concentration in Sample C was also determined by ion chromatography with a post-column reaction [ICS-1100 + PCM 520 + UVD-510, Thermo Fisher Scientific (Dionex)]. The concentration of I^- in Sample C was calculated by subtracting the IO_3^- concentration from the iodine concentration determined by ICP-MS. The percentage of each iodine species was calculated as the ratio of the species concentration to the total iodine concentration (that is, the sum of the iodine concentrations in Samples C, D, and E).

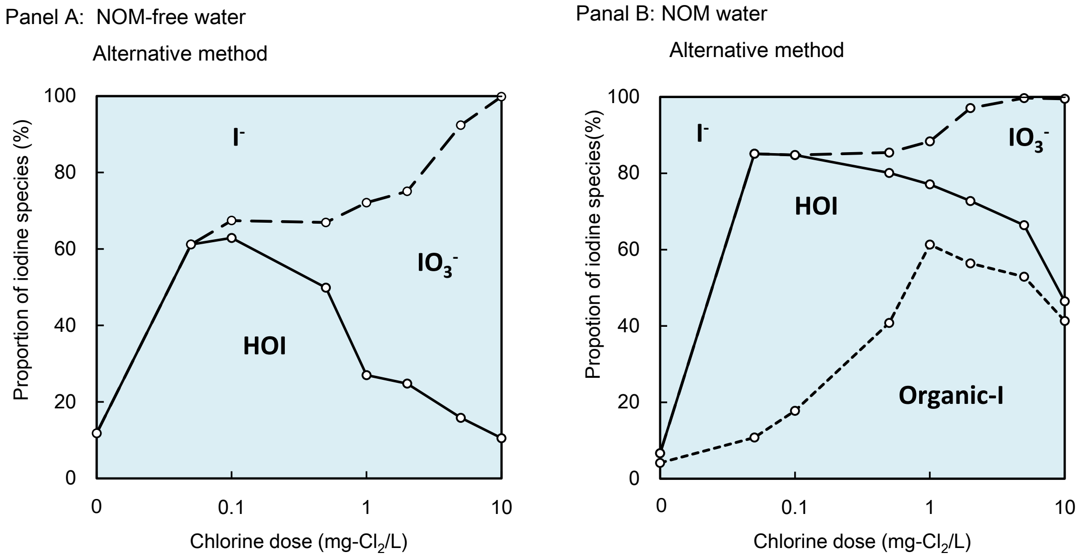

Figure S5. Proportion of iodine species in NOM-free (left) and NOM water (right) as a function of chlorine dose, as determined by the alternate method described here. Chlorine oxidation time, 10 min; initial I^- concentration in sample water, 10 μg-I/L; initial DOC concentration in NOM water, 1.5 mg-C/L; carbon contact time, 30 min.

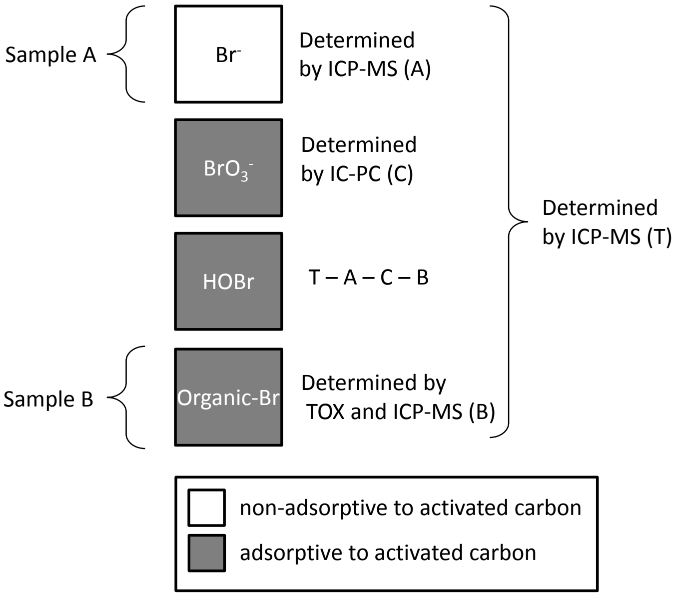

Figure S6. Image of bromine fractionation method

Section 4: Direct observation of iodine adsorbed on PAC particles

3.1. Preparation of PAC particles for cross-sectional observation

3.1.1. Target: HOI

Potassium iodide was added to NOM-free water at an iodine concentration of 10 mg-I/L. The water was first treated with chlorine (5 mg-Cl_2/L) to oxidize the iodine, and then 10 mg/L of PAC was added. After a 30-min carbon contact period, an aliquot of the water was centrifuged at 500 rpm (45 G) for 10 min to separate the PAC particles from the water. The separated particles were re-suspended in Milli-Q water, and a few drops of the suspension were placed on a silicon (Si) wafer, which was dried at 20 °C for 48 h.

3.1.2. Target: Organic iodine

Potassium iodide was added to NOM water (DOC = 10 mg-C/L) at an iodine concentration of 10,000 μg-I/L (the high iodine concentration was required to obtain sufficient signal intensity of iodine on the FE-EPMA described below). The water was first treated with chlorine (5 mg-Cl_2/L) to oxidize the iodine, and then 10 mg/L of PAC was added. After a 30-min carbon contact time, an aliquot of the water was centrifuged at 500 rpm for 10 min to separate the PAC particles from the water. The separated particles were washed with 0.08 mol/L KNO_3 solution to remove HOI, and the washed particles were centrifuged at 500 rpm for 5 min to separate the PAC particles from the wash solution. The separated particles were re-suspended in Milli-Q water, and a few drops of the suspension were placed on a Si wafer, which was dried at 20 °C for 48 h.

3.2. Focused ion beam sectioning of PAC particles

A Si wafer on bearing PAC particles was mounted with double-stick carbon tape (Nisshin EM Co., Tokyo, Japan) on the specimen holder of a focused ion beam (FIB) system (FB-2100, Hitachi, Tokyo, Japan). The surface of the PAC particles was coated with a 20-nm layer of platinum (Pt), to avoid charge-up effects, by means of ion sputtering equipment (JEC-1600, JEOL, Tokyo, Japan). A PAC particle was selected arbitrarily during real-time scanning-ion microscope observation, and then tungsten (W) was FIB-deposited on the particle for 20 min to prevent damage to the particle during FIB milling, which was performed at a beam energy of 40 kV (Figures S5 and S6-1). Deep trenches were cut around the PAC particle by means of gallium (Ga) FIB milling such that only a small cubic portion (a microsample) of the wafer with the PAC particle on top remained; a corner of the small cubic portion (a microbridge) was left to connect the microsample to the wafer (Figure S6-2). Subsequently, the specimen holder was tilted to 60°, and the bottom of the microsample was cut with a Ga FIB; as a result, the microsample was supported by a microbridge at one corner (Figure S6-3). A mechanical probe was inserted into the specimen holder, and the tip of the probe was welded to the microsample by means of FIB-assisted W deposition (Figure S6-4). After the microbridge was cut with a Ga FIB, the microsample was separated from the wafer and placed on a newly inserted wafer by means of W deposition (4 min). The newly inserted wafer was mounted on the sample holder of the FIB system by means of double-stick carbon tape, and then the mechanical probe was cut with a Ga FIB (Figure S6-5). About one-quarter of the PAC particle on the microsample was then cut away with a Ga FIB to leave a cut PAC particle, and then the other side of the cut PAC particle was cut away (Figures S4 and S6-6). The cut particle was coated with a 2-nm layer of Pt by ion sputtering to avoid charge-up effects during field emission electron probe microanalysis (FE-EPMA).

3.3. Observation of PAC particle by FE-EPMA

FE-EPMA is a nondestructive method used to determine the chemical composition of a small portion of a solid material. The Si wafer with the FIB-cut PAC particle was clipped with a sample holder for FE-EPMA observation of the particle cross-section. Mapping-scan chemical analysis was performed on the surface of the cross-sectioned particle in the FE-EPMA (acceleration voltage, 10 keV; irradiation current 5×10^{-8} A; dwell time, 80 ms).

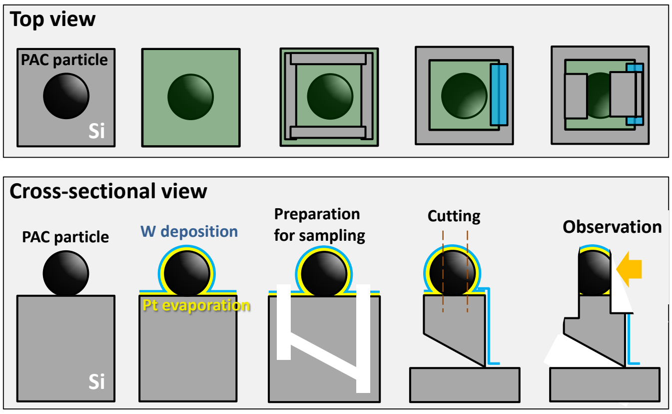

Figure S7. Schematic diagram of sample preparation for FE-EPMA observation.

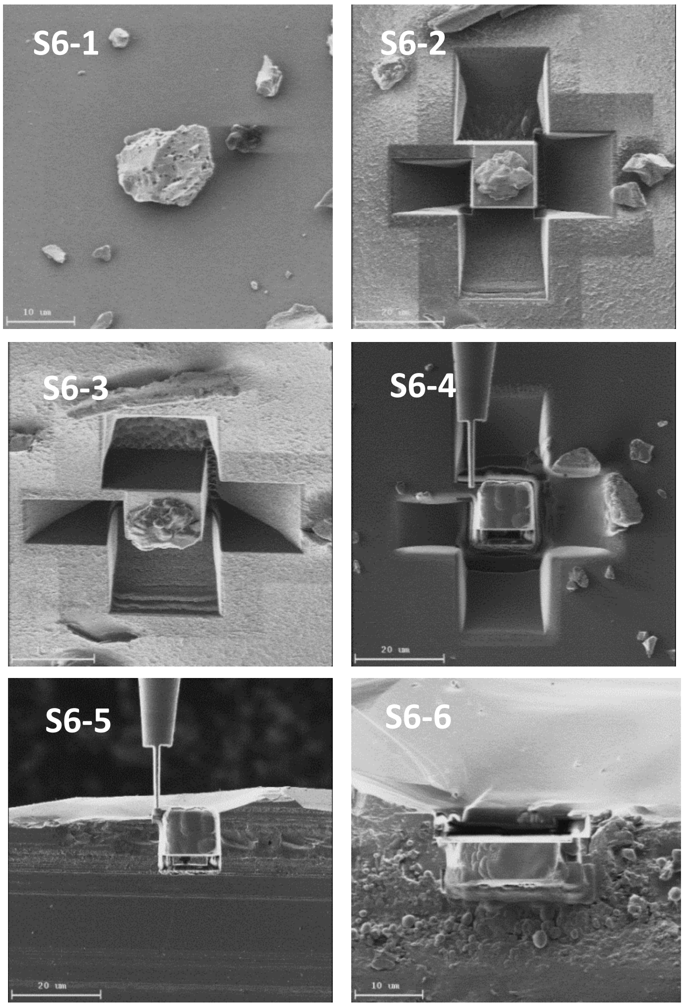

Figure S8. Microsampling and sectioning of a PAC particle using FIB milling: (S6-1) PAC particles were placed on a Si wafer; (S6-2) deep trenches were cut around the PAC particle by means of Ga FIB milling such that a small cubic portion (microsample) of the Si wafer with the PAC particle on top remained; (S6-3) the specimen holder was tilted to 60°; (S6-4) while the microsample was supported by a microbridge at one corner, a W probe was inserted into the specimen holder, and the tip of the probe was welded to the microsample; (S6-5) the microsample was placed on a newly inserted Si wafer; and (S6-6) a cut PAC particle was obtained.

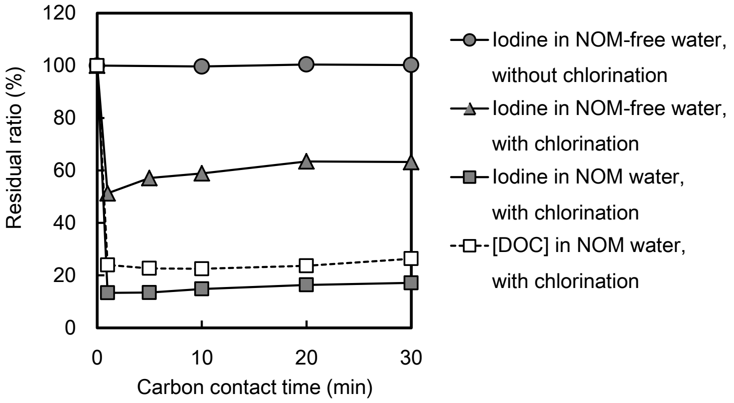

Figure S9. Changes in residual iodine ratio and DOC concentration with SPAC contact time, with and without prior chlorination. Chlorine dose , 1 mg-Cl$_2$/L; chlorination time, 10 min; SPAC dose, 100 mg/L; initial I^- concentration in sample water (both NOM water and NOM-free water), 10 µg-I/L; initial DOC concentration in NOM water, 1.5 mg-C/L.

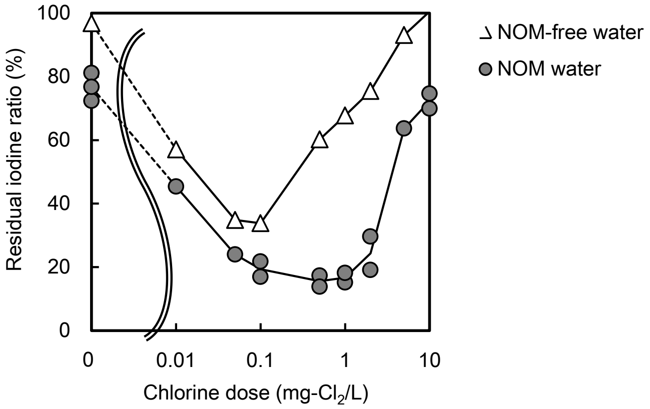

Figure S10. Effect of chlorine dose on adsorptive removal of iodine. SPAC dose, 100 mg/L; initial I^- concentration in sample water (NOM water and NOM-free water), 10 µg-I/L; initial DOC concentration in NOM water, 1.5 mg-C/L; chlorination time, 10 min; carbon contact time, 30 min.

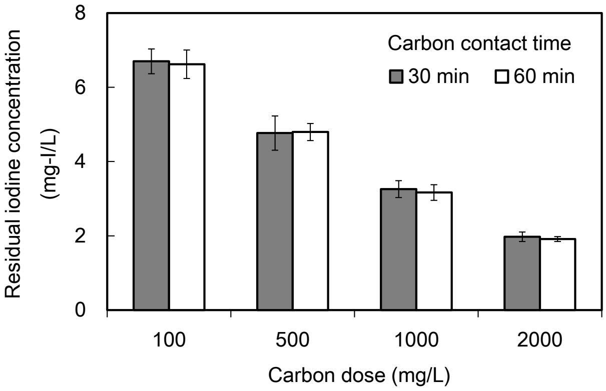

Figure S11. Comparison of the effects of carbon contact time on residual iodine concentration at carbon doses of 100–2000 mg/L. Chlorine (0.5 mg-Cl_2/L) was added to the NOM-free water 10 min before PAC was added.

Table S1. Ion concentrations (mmol/L) and conductivity (μS/cm)

	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	NO_3^-	Conductivity
Hakucho water	0.34	0.21	0.07	0.03	0.26	0.04	0.17	0.02	77-89

References

Tate, C.H., Chow, B.M., Clark, R.R., Grams, N.E. and Hashimoto, L.K., (1986) EPA Method Study 32: Method 450.1-Total Organic Halide (TOX), Environmental Monitoring and System Laboratory, USEPA, Cincinnati, Ohio, USA, http://www.epa.gov/nscep/index.html (accessed on 18/5/2014).