Electronic Supporting Information

Carbonaceous DBPs (THMs and HAAs) formation on Cl_2 and ClO_2 treatment of aqueous leachable fractions of soil-derived natural organic matter

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S1: Generation of Chlorine dioxide

The stoichiometry of the reaction is as follows.

$4NaClO_2 + 2H_2SO_4 \rightarrow 2ClO_2\uparrow + 2Na_2SO_4 + HCl + HClO_3 + H_2O$

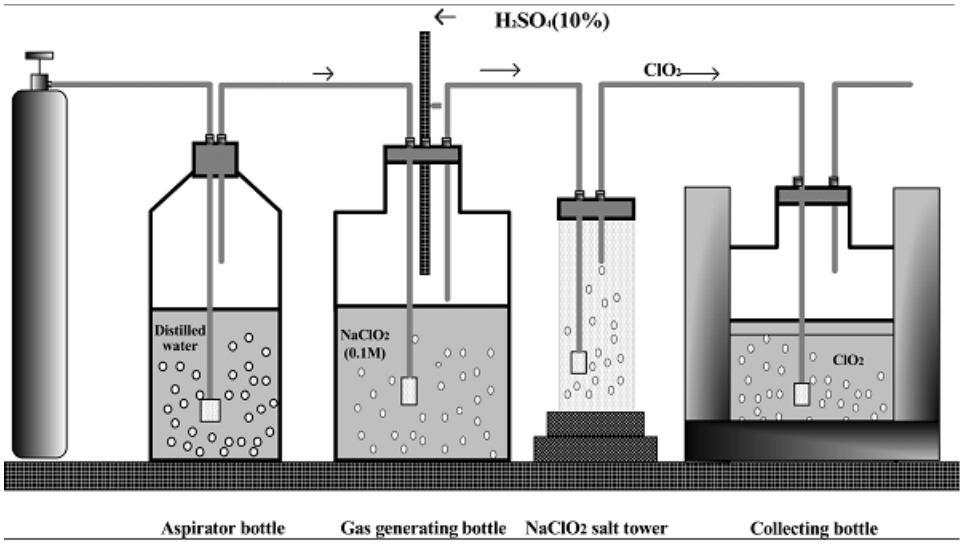

Fig. S1 Schematic of chlorine dioxide generation by the acid activation of $NaClO_2$

The reaction flask and gas scrubbing salt tower were filled with 500 mL 0.1M $NaClO_2$ solutions. 50 mL of sulphuric acid solution was added drop by drop to the reaction flask. The ClO_2 gas generated was purged by bubbling nitrogen gas through the solution. N_2 gas flow was maintained for 30 mins after the completion of H_2SO_4 acid addition. The chlorine dioxide gas driven off by sparging with nitrogen gas was carried through three traps kept in series as shown in **Fig. S1** and finally absorbed into the ice-cold distilled water. The concentration of ClO_2 aqueous solution generated by this way was 1000-2000 mg/L. At STP, the solubility of chlorine dioxide in water is 3.0 g/L and decreases with increase in temperature. The chlorine dioxide solutions were standardized by Iodometric titration method, and its concentration was determined at the beginning of each experiment. Chlorine dioxide solutions were kept in an airtight amber color bottle at 4^0C while not in use to avoid its decomposition.

S2: Soil Sampling

Soil samples were collected from different locations along the Bay of Bengal coast is depicted in the land use map Fig. S1. About 100 gm of soil samples from a 20 X 20 cm2 area were collected from each location with the help of a stainless steel scoop after discarding the 5 cm top surface soil. The soil samples were dried using a lyophilizer, ground to 63 µm and stored in a desiccator until use. Samples were pooled and homogeneously mixed together to make the composite bulk sample for organic matter extraction.

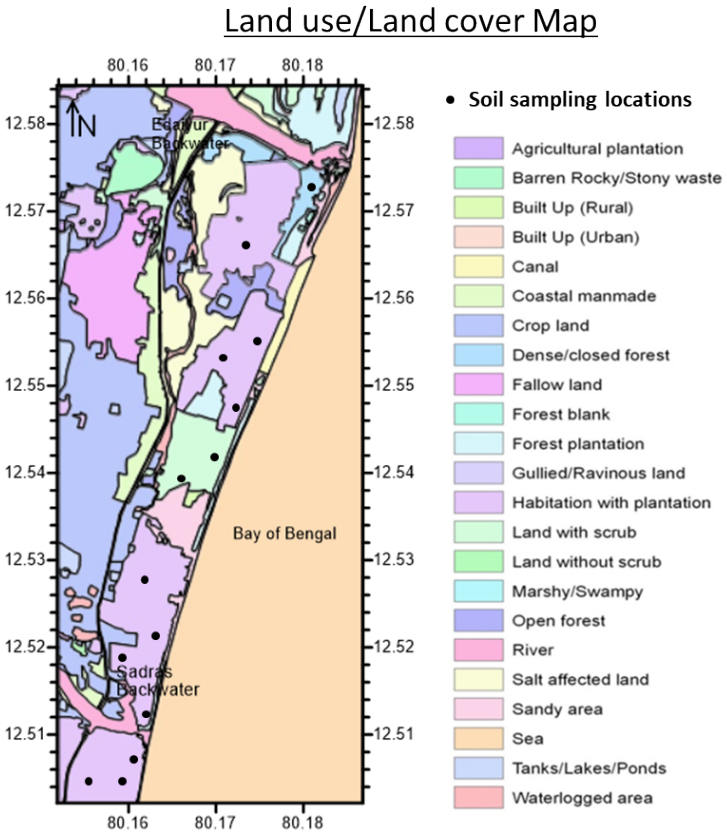

Fig. S2 Soli sampling locations and soil type descriptions

S3: Extraction of Organic matter from soil

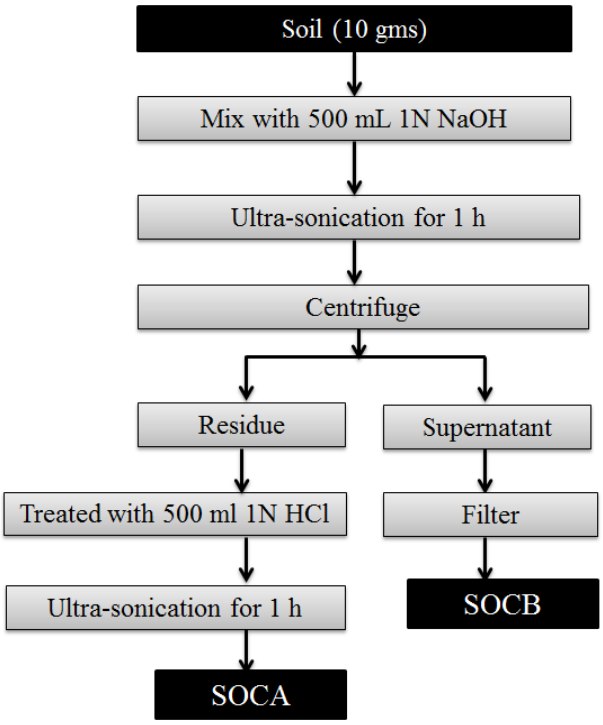

Fig. S3 Schematic of separation of alkali (base) leachable and acid leachable organic content (OCA and OCB)

S4: Fractionation of NOMs

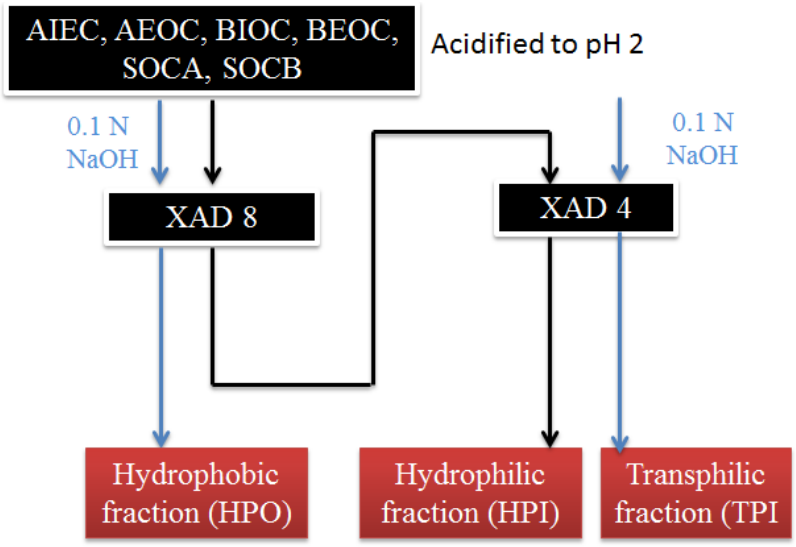

Fig. S4 Fractionation of organic content in the aqueous samples based on XAD-8 and XAD-4 resin adsorption

S5: THMs Analysis

A mixture of four THM standards and a mixture of nine HAAs standards were purchased from Sigma Aldrich. Working standards of THMs for calibration were prepared by spiking into deionized water to get a series of concentration varied from 0.1 to 100 µg/L of each THMs species. USEPA method 551.1 for THMs and 552.2 for HAAs with minor modifications was followed for sample preparation and gas chromatography-electron capture (GC-ECD) measurement to quantify THMs and HAAs. Screw cap glass vials (10 mL) were used for the liquid-liquid extraction. Water samples (5 mL) were transferred to the glass extraction vials using an auto pipette. To each 5 mL of water sample in the extraction vial, 2 mL of pentane was added gently. Then 2 g of reagent grade sodium sulfate (Na_2SO_4) was added to the extraction vial to enhance the partitioning of the THMs into the organic phase and also to minimize the solubility of pentane in water samples. Extraction vials were closed tightly, laid horizontally on a shaker platform, and shaken at 300 rpm for 15 min. After shaking, the vials were allowed to settle for at least 10 min, and 2 mL of the upper layer of pentane was transferred using an airtight glass syringe into a 2 mL GC vials for subsequent analyses. Analysis of THMs was carried out with a gas chromatograph attached with an electron capture detector (ECD) attached with an auto-sampler (GC-1110, Thermo-Scientific, India), the ECD detector is highly sensitive to haloorganics. Identification of the four THMs species was confirmed by injecting individual THM standards and identified by the retention time. Quantification of the THMs species was carried out by external standard calibration, and Iris software was used for chromatogram peak integration. The capillary GC column CB-5 column with ID, 0.25 mm, film thickness, 0.25 µm and length, 30 m (Cyber Lab, USA) was used both in GC-MS/MS and GC-ECD with same operating conditions. For the separation of four THMs species, the injection and detector temperatures were maintained at 150°C, and 260 °C, and oven temperature program was set as follows: 30 °C-10 min - @3^0C/min - 41 °C – 6 min - @ 5^0C/min - 81°C – 0 min - @ 25^0C/min – 180°C 6 min. **Fig. S4** shows an overlaid chromatogram of various samples and standards analysed by GC-ECD. The injection was set as split mode with split ratio 1:5 with an injection of 2 µL of pentane extract. Ultra-high pure (99.999%) nitrogen gas was used both as a carrier and makeup gas for GC-ECD, whereas ultrapure helium gas was used as GC-MS carrier gas. A minor change in the retention time and detector response is expected over a period of time for GC analysis, and relevant details would be mentioned in the respective chapter.

S6: HAAs Analysis

A mixture of nine HAAs standards was purchased from Sigma Aldrich. The preparation of HAAs calibration standards was similar to that of THMs. USEPA method 552.2 with some modifications was employed for the liquid-liquid extraction, analysis, and quantification. This method is based on the acid catalyzed esterification of the HAAs before analysis by GC. Briefly, to the 90 mL of water sample in a glass extraction vial, 2 mL of concentrated (98%) H_2SO_4 was added to the water to convert the acetates to their corresponding acids. HAAs were extracted from the aqueous solution with 5 mL of methyl - tertiary butyl ether (MTBE) by shaking vigorously for 15 min at 300 rpm in a mechanical shaker. Prior to MTBE addition, about 16 g anhydrous sodium sulfate was added to the extraction vial to enhance the partitioning of the HAAs into the organic phase and also to minimize the MTBE water solubility. The extraction vials were allowed to settle for at least 10 min to separate

the two phases. After settling, 3 mL of the upper MTBE layer was transferred to a 10 mL glass vial for the derivatization of HAAs to their corresponding esters. For the esterification, 1mL of 10% acidified methanol was added to the MTBE extract and allowed to react for 2 hours at 50^0C in a water bath for the complete conversion of HAAs to their corresponding methyl esters. The resultant reaction mixture was treated with 6 mL of 15% anhydrous sodium sulfate solution, and the upper organic layer was transformed to a vial containing 4 mL of saturated sodium bicarbonate solution to neutralize the solution. Finally, 2 mL of the organic upper layer was transferred to a GC vial for analysis. The same GC-MS/MS, GC- ECD and GC column that was used for THMs analysis were used for identification and regular analysis of HAAs as well. The GC oven temperature program followed was, initial oven temperature: 35°C, hold time 15 mins, 5°C/min up to 75°C held for 10 mins, 5°C/min up to 100 °C, and held for 5 min, and 5 °C/min up to 135°C held for 2 mins, and 25^0C/min up to 200^0C and held for 0 min. Total run time was 57 mins. Injection and detector temperature were maintained at 150°C and 260°C respectively. **Fig. S5** and **Fig. S6** depict the GC-MS and GC-ECD chromatogram respectively for the HAAs analysis.

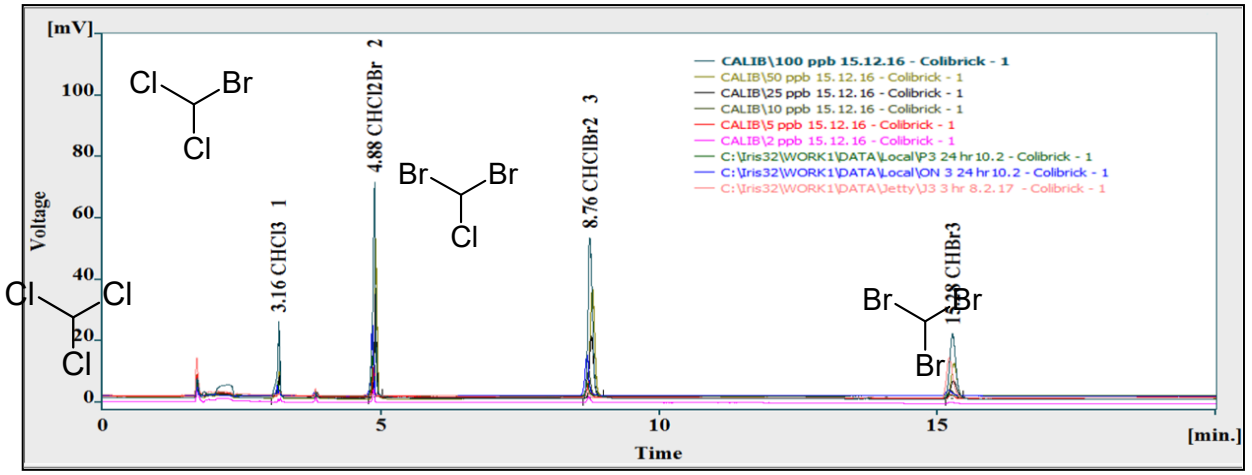

Fig. S4 Overlay chromatogram of THMs obtained for various samples and standards analyzed by GC-ECD

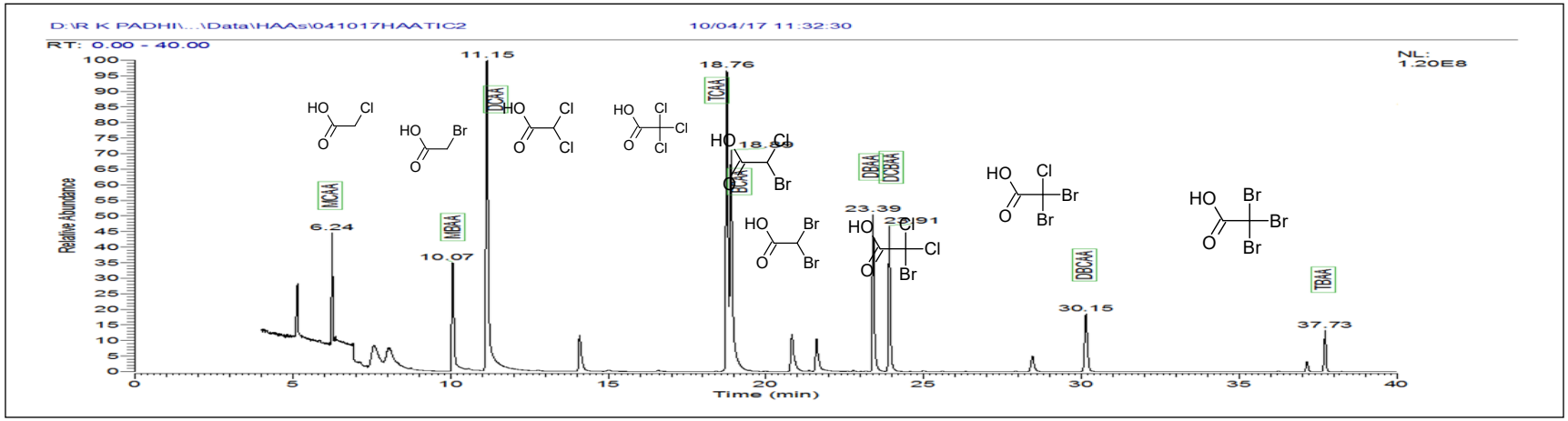

Fig. S5 GC-MS total ion chromatogram for the identification of HAAs species

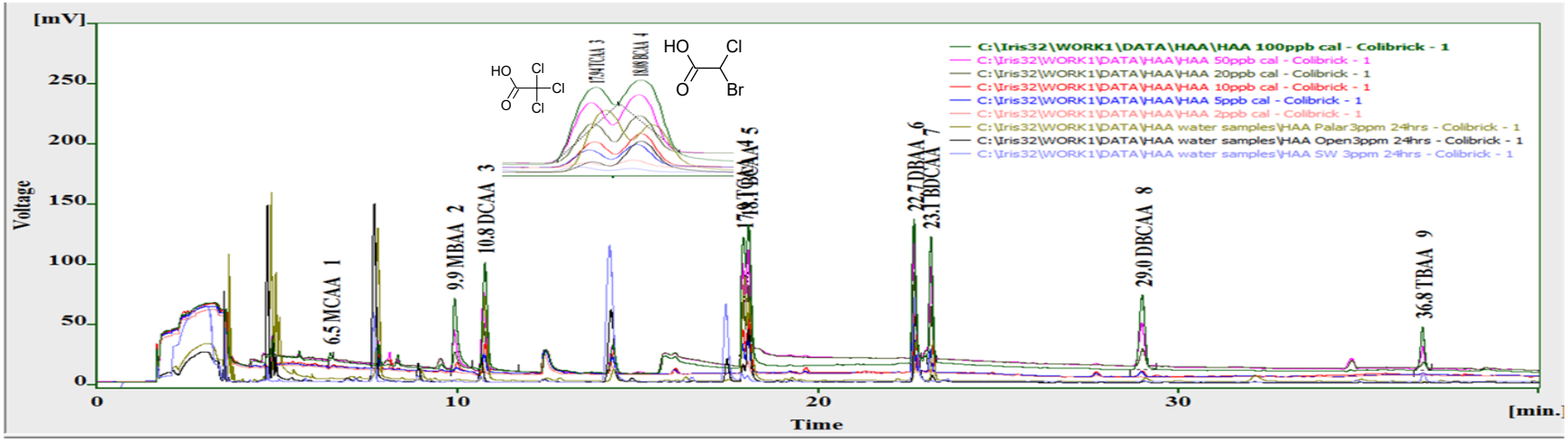

Fig. S6 chromatogram of HAAs analyzed for standards and samples