Supplemental Material

Spatiotemporal characteristics of organic contaminant concentrations and ecological risk assessment in the Songhua River, China

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1. Analysis of PAHs

1.1 Water sample pretreatment

A 1L water sample was placed into a 2L separator funnel. 30g NaCl was then added and dissolved, followed by 50mL dichloromethane. The funnel was shaken (10min) and allowed to settle (5min). The organic phase was transferred to a flask. This extraction process was repeated twice and the extracts combined. Next, 3g Na_2SO_4 was added to the organic phase and agitated; after twenty minutes, the solution was filtered and transferred to a rotary evaporator until 3mL remained. This was further condensed to 1mL by N_2 stream stripping. 10mL of n-hexane was put into the extract and re-condensed to 1mL, again by N_2 stream stripping. The extract was put through a silica gel chromatograph, activated by 10mL acetone-n-hexane and 10mL of n-hexane and cleaned using 10mL of 10% acetone-n-hexane. 1mL eluate condensed by N_2 stream stripping with addition of 10μL of surrogate perdeuterated naphthalene, perdeuterated acenaphthene, perdeuterated chrysene, perdeuterated phenanthrene and perdeuterated fluoranthene (10μg/mL). Finally, the solution was supplemented to 1.0mL for GC-MS determination.

1.2 GC-MS analysis

PAH concentrations were determined by a GC-6980N/MS-5973N, Agilent Technologies Inc. DB-5MS chromatogram column (J&W Scientific; 30m×0.32mm, 0.25μm film thickness). Column temperature was kept at 353°K for 2min and

increased to 563°K for an additional 5min. The instrument was operated in selected ion mode (SIM) with a detection range of ~35-400m/z. Additional details of the analytical methods can be found in (MEP, 2002). Samples were analyzed for 8 PAHs [pyrene (PYR); fluorene (FLU); chrysene (CHR); anthracene (ANT); naphthalene (NAP); fluoranthene (FLA); acenaphthene (ACP); phenanthrene (PHE)].

1.3 Precision and accuracy

All analytical data were subjected to a strict QA/QC. Blank samples were included and all concentrations were blank corrected. All concentration data were the average of three replicates for each sample. 1L of pure water was prepared, and then added with 50ng perdeuterated PAH standard solution (solvent is acetone). After this, pretreatment and analysis procedure of water sample were the same as the content mentioned above. The recovery of each PAH in standard solution and the relative standard deviations (RSDs) were 85%-95% and 4%-8%, respectively.

2. Analysis of Phenols

2.1 Water sample pretreatment

A 1L water sample was placed into a 2L separator funnel, and the solution's pH was adjusted to 2-3 using 6mol/L HCl solution. 30g NaCl was added and dissolved, 50mL dichloromethane was added, the vessel was then shaken for 10min and allowed to stand for 5min. The dichloromethane fraction was transferred to a flask. This process was repeated and extracts combined. 3g Na_2SO_4 was added and the solution

agitated. After standing for 20min, the solution was filtrated and transferred to a rotary evaporator for concentration to 1mL. This volume was then transferred to a K-D concentrator using dichloromethane and condensed to 0.5mL using N_2 stream stripping. 100uL of BSTFA was added to the solution after standing for 1h at room temperature. Finally, the solution was added with 10mL of perdeuterated naphthalene (surrogate, purity 99%) and reconstituted in 1mL of dichloromethane for quantification.

2.2 GC-MS analysis

Phenolic compound concentrations were determined by a GC-6980N/MS-5973N, Agilent Technologies Inc. DB-5MS chromatogram column (J&W Scientific; 30m×0.32mm, 0.2μm film thickness). Column temperature was kept at 328°K for 2min, increased to 378°K, then 478°K, and finally 578°K for 5min. The pressure of He gas was kept at 40kPa for 5min, then increased to 70kPa and kept for 5min. The instrument was operated in selected ion mode (SIM) with a detection range of ~35-400m/z. Additional details of analytical methods can be found in (MEP, 2002). Samples were analyzed for 8 phenols [phenol (PHN); 2-nitrophenol (2-NP); 4-nitrophenol (4-NP); 2-chlorophenol (2-CP); 2,4-dichlorophenol (2,4-DCP); 2,4-dimethylphenol (2,4-DMP); 2,4,6-trichlorophenol (2,4,6-TCP); 4-chloro-*m*-cresol (4-CMC)].

2.3 Precision and accuracy

All analytical data were subjected to a strict QA/QC. Blank samples were included and all concentrations were blank corrected. All concentration data were the average of three replicates for each sample. 50μL of the mixed standard solution of 2,4-Dichlorophenol and 2,4-Dinitrophenol was added into 1L of pure water, and then it was transferred to 2L separator funnel. After this, pretreatment and analysis procedure of water sample were the same as the content mentioned above. The recovery of phenolic compound in standard solution and the relative standard deviations (RSDs) were 98%-101% and 1.7%-6.7%, respectively.

References

MEP. 2002. Monitoring and analysis methods for water and wastewater (Chinese). Fourth ed. China Environmental Science Press, Beijing.