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Innovative approach to reveal source contribution of dissolved organic matter in a complex river watershed using end-member mixing analysis based on spectroscopic proxies and multi-isotopes

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Dissolved organic matter(DOM) in river watersheds dynamically changes based on its source during a monsoon period with storm event. However, the variations in DOM in urban and rural watersheds that are dominated by point and non-point sources have not been adequately explored to date. We developed an innovative approach to reveal DOM sources in complex river watershed systems during pre-monsoon, monsoon, and post-monsoon periods using end-member mixing analysis(EMMA) by combining multi-isotope values(δ13C-DOC, δ15N-NO3, δ18O-NO3) and spectroscopic indices(fluorescence index[FI], biological index[BIX], humification index[HIX], and specific UV absorbance[SUVA]). Several potential end-members of DOM sources were collected, including top-soils, groundwater, plant group(fallen leaves, riparian plants, suspended algae), and different effluents(cattle and pig livestock, agricultural land, urban, industry facility, swine treatment facility and wastewater treatment facility). Concentrations of DOC, DON, NO3-N, and NH4-N increased during the monsoon period with an increase in the input of anthropogenic DOM, which have higher HIX values owing to the flushing effect. The results of EMMA indicate that soil and agricultural effluents accounted for a substantial contribution of anthropogenic DOM at varying rates based on seasons. We also found that results of EMMA based on combining spectroscopic indices and δ13C-DOC isotope values were more accurate in tracing DOM sources with respect to land-use characteristics compared to applying only spectroscopic indices. The positive relationship between FI, BIX and δ15N-NO3 were revealed that nitrate would be decomposed from DOM affected by intensive agricultural activities. In addition, consistent with the EMMA results, the molecular composition of the DOM was clearly evidenced by a large number of CHON formulas, accounting for over 50% of the total characterized compounds, including pesticides and pharmaceuticals used in agriculture farmland and livestock. Our results clearly demonstrated that EMMA based on combing multi-stable isotopes and spectroscopic indices could be trace the DOM source, which is important for understanding changes in the DOM quality, and application of nitrate isotopes and molecular analysis supports in-depth interpretation. This study provides intuitive techniques for the estimation of the relative impacts of DOM sources in complex river watersheds, which can be verified in various ways rather than relying on a single technique approach.