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Beyond NOM: Halogenated Organic Matter as an Overlooked Distinct Carbon Pool in Megacities

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Organic halogens comprise a chemically diverse class of compounds derived from both natural and anthropogenic processes, many of which are environmentally persistent and toxic. Rapidly urbanizing megacities have become hotspots for the production and transformation of organic halogens, driven by widespread chlorine-based disinfection and extensive use of halogenated chemicals in water treatment, domestic sanitation, agriculture, and industry. Massive and continuous halogen inputs are progressively reshaping the composition of conventionally defined natural organic matter (NOM), promoting the formation and accumulation of halogenated organic matter (XOM) that now permeates wastewater effluents, urban runoff, estuaries, and coastal waters. The shift from conventionally defined NOM to an anthropogenically influenced carbon pool enriched in organic halogens, represents an emerging dimension of global change in megacities, altering the biogeochemical behavior of organic carbon in ways that remain largely unrecognized.

To address this gap, water samples from diverse environmental sources, including wastewater effluents treated as constrained point sources and urban runoff associated with different land uses, were collected across the Great Bay Area. Combustion Ion Chromatography was used to quantify XOM. Fourier-transform Ion Cyclotron Resonance Mass Spectrometry (FT-ICR MS), coupled with halogenated compound formula assignment, was used to identify the molecular composition and signatures of XOM. Our results showed XOM concentrations in urban runoff were lower than in wastewater effluents but remained substantially elevated relative to natural reference materials. Catchments dominated by artificial land use consistently exhibited higher XOM levels than forested areas. FT-ICR MS further revealed that halogenated compounds associated with disinfection sources exhibited higher nominal oxidation states of carbon than both naturally occurring halogenated molecules and their non-halogenated analogues, indicating that halogen incorporation fundamentally alters carbon redox characteristics and potentially reduces microbial energy yields during further oxidation. These results demonstrate that XOM accumulates as a distinct yet overlooked carbon pool in megacities, influencing halogen loadings, NOM cycling, and downstream ecological processes. Defining the biogeochemical boundaries between XOM and NOM, and establishing the ecological roles and traceability of XOM, are therefore critical for anticipating how ongoing urbanization and disinfection practices will reshape carbon cycling in megacity ecosystems in the decades ahead.

