

## Relation of land cover in river basins to fluorescent dissolved organic matter and iron flocculation in estuaries

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This study aimed to reveal the effect of land cover in river basins and dissolved organic matter (DOM) on dissolved Fe flocculation in estuaries. We collected river water samples at 30 sampling sites with different upstream land cover compositions in Northeast Japan. Seawater mixing experiments were then performed using the collected river water samples and artificial saline water to quantify the degree of flocculation of dissolved Fe under the high salinity conditions. The chemical property of DOM was also characterized by fluorescence spectra. The dissolved Fe (< 0.45  $\mu\text{m}$  fraction) concentrations in the river water samples ranged from 6.0 nM to  $2.1 \times 10^3$  nM, whereas dissolved Fe concentrations after seawater mixing substantially decreased ranging from 0.53 nM to 450 nM. The Fe transport capacity defined by non-flocculated fraction was determined from 1.5% to 83%. In addition, the non-flocculated dissolved Fe concentration showed significant positive correlations to the fluorescence intensities of all the fluorophores identified by parallel factor analysis (PARAFAC). Fe transport capacity was correlated positively to the fluorescence intensity ratios of fulvic acid-like fluorophores but negatively to those of humic and protein-like fluorophores. Further, non-flocculated dissolved Fe concentration correlated positively to the land cover ratio of cultivated land and urban land, although Fe transport capacity correlated positively to the land cover ratio of vegetation and negatively to those for cultivated land. Therefore, the findings in this study indicated that land cover in river basins and resultant DOM characteristics are important determinants for Fe transport from river to coastal area, and DOM originated from vegetation potentially enhances Fe transport from rivers to the ocean.

**Keywords:** Fe flocculation in estuary, fluorescence emission-excitation matrix, dissolved organic matter, fulvic acid, land cover, vegetation

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