



Spectroscopic analysis of N-compounds in various fractions of riverine dissolved organic matter

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N-containing organic compounds represent the second most abundant reservoir of nitrogen of earth. Geochemical organic nitrogen occurs mainly in soil organic matter in terrestrial pools and in dissolved or particular organic matter in aquatic ones. Natural organic matter (NOM) is a ubiquitous component of natural waters with concentration up to 60 mg/l. Organic substances are transported from the continent to coastal marine environments via river discharge and contribute significantly to offshore water. River systems thus play a major role in the global biogeochemical cycle of nitrogen. Rivers are dynamic ecosystems, which integrate different inputs related to drainage basin and autochthonous production. Thus riverine dissolved OM (DOM) exhibits a large diversity in composition involving different reactivity in environmental processes. However, in spite of its importance and likely due to its refractory character, the precise chemical structure and origin of NOM is still partly unidentified. Characterization of organic nitrogen is still incomplete, the chemical structure and origin of nitrogen compounds remaining widely unknown. Recent studies, using ^{15}N NMR spectroscopy, pointed to the occurrence of amide functions in these natural environments, thus suggesting that N is engaged in polar building blocks (1, 2). The purpose of this study was to investigate the forms of organic nitrogen in different fractions of riverine DOM. In a previous work, a number of pyrolysis products were identified for each fraction, some of them being specific of macromolecular source. Differences in abundance of N-containing pyrolysis products are observed in spite of similar N contributions. Moreover the molecular structure of these compounds, which are mainly nitrogen- and oxygen- containing molecules, does not allow ascertaining their origin. These observations led to question the occurrence of possible different nitrogen-

macromolecule sources for the fractions. The major biological sources of organic nitrogen such as proteins, amino sugars or tetrapyrrole pigments involving differences in the main nitrogen functionality, the aim of the present work was to determine the nitrogen functional groups present in the DOM fractions by using additional analytical approach, including two spectroscopic methods: X-ray photoelectron spectroscopy (XPS) and solid state ^{15}N NMR. The use of XPS to derive information on the chemical environment of one atom was only scarcely applied to the chemical analysis of organic matter. Combination of these two methods reveals the presence of different functionality of nitrogen (amide, amine, and N-heterocycle), with variation in relative contribution depending on the considered fraction. Moreover it appears that Curie point pyrolysis does not account for the presence of the nitrogen in macromolecules with the same efficiency depending on the functional group involved.

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