

# MOLECULAR DISTRIBUTION OF DICARBOXYLIC ACIDS AND RELATED POLAR COMPOUNDS IN THE RHONE RIVER AND COASTAL MEDITERRANEAN SEA WATER IN RELATION WITH PHOTOCHEMICAL AND BACTERIAL PROCESSES

R. Sempéré<sup>1</sup>\*, M. Tedetti<sup>1</sup>, B. Charrière<sup>1</sup>, M. Abboudi<sup>1</sup>, F. Joux<sup>2</sup>

<sup>1</sup> Laboratoire de Microbiologie Géochimie et Ecologie Marines, UMR CNRS/INSU 6117, Case 907, Centre d'Océanologie de Marseille, Université de la Méditerranée, 13 288 Marseille Cedex 9 France - sempere@com.univ-mrs.fr

<sup>2</sup> Laboratoire d'Océanographie Biologique de Banyuls. Université Paris 6, CNRS UMR 7621. Banyuls-sur-mer, France

## Abstract

We recently developed a new method for extraction and detection of diacids in marine waters and found that such free dissolved organic compounds may comprise up to 2.5% of dissolved organic carbon (DOC) (1). Here, we report for the first time, molecular distribution of diacids and related polar compounds in North western Mediterranean Sea and Rhone River samples. Additional laboratory controlled experiments indicated that biological process largely controlled molecular distribution of diacids in marine DOM although they can be quantitatively produced through photochemical oxidation reactions of unsaturated long chain fatty acids.

*Keywords* : *Organic Matter, Bacteria, Rhone Delta, Chemical Speciation.*

$\alpha$ ,  $\omega$  dicarboxylic acids are abundant short chain intermediate reactions products found in aerosol, rainwater and snow samples. They are produced in the atmosphere by incomplete combustion of fossil fuels or fresh biomass as well as from the ozonolysis and photooxidation of natural and anthropogenic organic compounds in the atmosphere. The main sink of these short chain diacids remains the photomineralization process and in cloud scavenging since shorter chain compounds may act as cloud condensation nuclei (2). This process can in turn affect the radiative earth balance.

We recently developed a new method for extraction and detection of diacids in marine waters and found that such free dissolved organic compounds may comprise up to 2.5% of dissolved organic carbon (DOC) (1). Briefly, the seawater sample was first acidified and then passed through an activated charcoal column to adsorb the dicarboxylic acids. Diacids were then derivatized with BF<sub>3</sub>/n-butanol to dibutyl esters, and determined using a capillary GC/MS. Here, we report molecular distribution of diacids and related polar compounds in North western Mediterranean Sea and Rhone River samples which is the main supplier of dissolved organic matter to the whole Mediterranean Sea (3).

Our results indicated significant changes in the molecular distribution between atmospheric rainwater and aerosol samples and aquatic samples. Additional laboratory controlled experiments, indicated that biological process largely controlled molecular distribution of diacids in marine DOM although they can be quantitatively produced through photochemical oxidation reactions of unsaturated long chain fatty acids (4).

In natural waters, many photochemical reactions are driven by  $\cdot$ OH radicals, which is one of the most reactive oxidants. Major sources of  $\cdot$ OH radicals in natural waters are the nitrate (NO<sub>3</sub><sup>-</sup>) and nitrite (NO<sub>2</sub><sup>-</sup>) photolysis, initiated by UV-B and UV-A (315-400 nm), respectively, as well as the photolysis of colored dissolved organic matter (CDOM), initiated by both UV-B and UV-A. Photochemical oxidation reactions may substantially modify molecular distribution and bacterial availability of dissolved organic compounds in natural waters and then play a significant role in aquatic carbon cycle. In this study, we also assessed under laboratory controlled conditions, the direct and hydroxyl radical ( $\cdot$ OH)-induced photochemical production of low molecular weight (LMW) dicarboxylic acids and related compounds (C<sub>2</sub>-C<sub>9</sub>) from oleic acid (cis-9-octadecenoic,  $\cdot$ 9C<sub>18</sub>) in pure, fresh and marine solutions. Additional laboratory biodegradation experiments indicated that the molecular distribution as well as their relative abundance within the DOC reservoir of dicarboxylic acids are the result of an equilibrium between bacterial assimilation, phytoplankton releases and photochemistry. Here we discuss about the sources and sinks of dicarboxylic acids in aquatic waters.

## References

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