

## The role of polyphenols on the Fe chemistry in seawater

ARIDANE G. GONZÁLEZ<sup>1</sup>, J. MAGDALENA SANTANA-CASIANO<sup>1</sup>, MELCHOR GONZÁLEZ-DÁVILA<sup>1</sup>, NORMA PÉREZ-ALMEIDA<sup>1</sup>, GERALDINE SARTHOU<sup>2</sup>

<sup>1</sup>Instituto de Oceanografía y Cambio Global, IOCGA.  
Universidad de Las Palmas de Gran Canaria, ULPGC.  
aridane.gonzalez@ulpgc.es;  
magdalena.santana@ulpgc.es;  
melchor.gonzalez@ulpgc.es; norma.perez@ulpgc.es.

<sup>2</sup>CNRS, Université de Brest, IRD, Ifremer, UMR 6539  
LEMAR, IUEM. geraldine.sarthou@univ-brest.fr

Iron is an essential micronutrient for phytoplankton and can limit primary production in the ocean and its chemistry is highly controlled by interactions with organic complexes (> 99%). Within the great variety of organic ligands produced by marine diatoms, polyphenols are exudated under stress conditions.

Among these polyphenols, (±) – catechin, sinapic acid, and gallic acid showed the ability to reduce Fe(III) to Fe(II) in seawater, making possible the persistence of Fe(II). In this sense, (±) – catechin and sinapic acid favoured the reduction of Fe(III) to Fe(II) in a pH-dependent process. In the presence of (±) – catechin, the Fe(III) reduction rate,  $\log k'$  ( $k'$ ,  $s^{-1}$ ) was  $-6.15$  at pH 8.0 and  $-3.79$  at pH 6.0, in seawater. In the presence of sinapic acid,  $\log k'$  was  $-6.57$  at pH 8.0 and  $-3.90$  at pH 6.0.

In addition, these three polyphenols are also able to complex Fe and it has been studied via kinetic and titration approaches. The results demonstrated that these three polyphenols are weak L<sub>2</sub>-type Fe-binding ligands according to the conditional stability constant, computed by using the kinetic approach ( $\log K'_{FeL} = 8.86 - 9.2$ ), where the formation rate constant ( $k_f$ ) was  $3.1 \cdot 10^5 - 4.2 \cdot 10^5 M^{-1} s^{-1}$  and the dissociation rate constant ( $k_d$ ) was  $2.43 \cdot 10^{-4} - 4.4 \cdot 10^{-4} s^{-1}$ . The conditional stability was also computed from the titration approach with  $\log K'_{FeL}$  from 8.6 to 9.5. These studied ligands also regenerated Fe(II) in seawater from 0.05% to 11.92%.

The results demonstrated that polyphenols, exudated by microalgae, should be taken into account in order to study the biogeochemical cycle of Fe. This current work also increases our knowledge about the role of individual organic binding ligands within the bulk of organic matter in the ocean on the Fe chemistry.