FINAL REPORT PROGRAM LEFE

Program LEFE/ Cyber	réévaluation de la labilité biotique et abiotique de la Matière Organique Terrestre rejetée par les fleuves et les rivières en MER (Acronyme : MORTIMER)	Years 2013-2014 and 2015-2017

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- *MALINA Franco-Canadian Program (ANR, NASA, LEFE-Cyber)*
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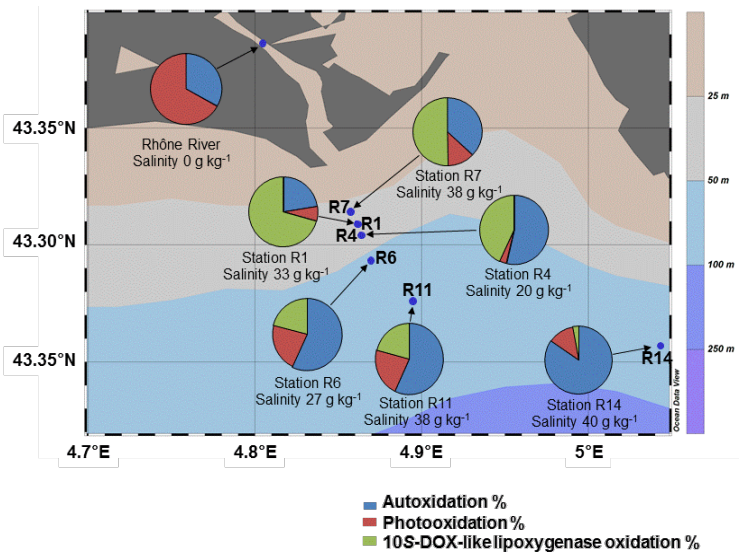
Context: While recent research has shown its importance in the degradation of terrestrial particulate organic matter (TPOM) in Arctic rivers, the mechanisms involved in the induction of autoxidation and biodegradation in coastal waters remained unclear.

Objectives: Evaluate the mechanisms that induce intense autoxidation (free radical oxidation) and biodegradation of in river-to-ocean gradients across a diverse suite of high to low latitude.

Results: Using new lipid tracers specific to the degradation of terrestrial higher plants at the mouth of the Rhône River, we confirmed the role played by autoxidation in the degradation of terrestrial POM (TPOM) in estuaries. As in the Beaufort Sea, autoxidation rates and salinity levels appeared to be correlated well within the river plume in the Mediterranean Sea. We identified for the first time the involvement of lipoxygenase (LOX) activity in the induction of autoxidation in transitional waters. The observation of unusual profiles of palmitoleic acid oxidation products and the presence of jasmonic acid in suspended particulate matter (SPM) collected close to the Rhône River and from the Mackenzie and Amazon river plumes was attributed to strong LOX activity. We showed the role played by salinity in the induction of this LOX activity (Illustration 1) and provided an explanation for the differences in autoxidation levels. At high latitudes, lower temperatures and irradiances favor photooxidative damage to higher plant debris and, consequently, hydroperoxide production. These high hydroperoxide contents strongly contribute to LOX activation (Illustration 2). The high resulting LOX activity enhances alkoxyl radical production and thus autoxidation. On the contrary, at low latitudes, photooxidative effects are limited, while riverine autoxidation is favored. The resulting higher hydroperoxide content of TPOM may, as a consequence, contribute to a high level of LOX activity and autoxidation. In temperate zones, the low riverine photooxidative and autoxidative damage induces only moderate increases in autoxidation in mixed waters. Preliminary in vitro *experiments also suggested that the intense biodegradation of TPOM observed in fluvial plumes may result from the selection of bacteria adapted to the degradation of this substrate in the salinity gradient and to the involvement of priming effect.*



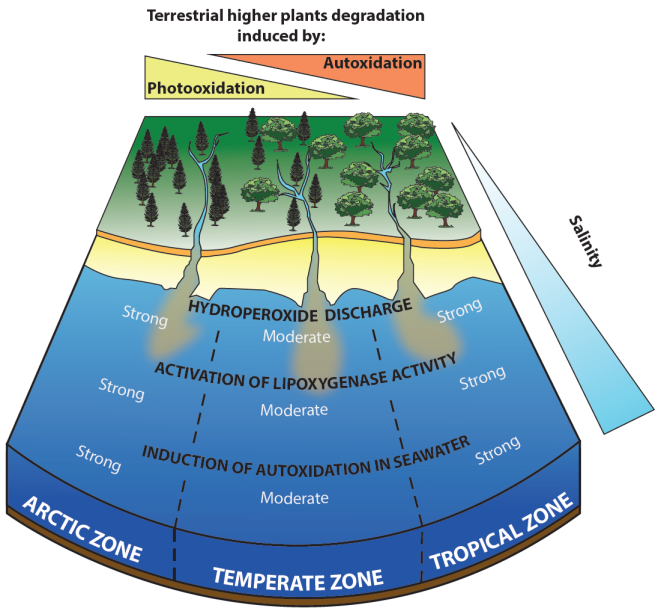


Illustration 1: Estimation of the relative part played by autoxidation, photooxidation and lipoxygenase in the degradation of palmitoleic acid in suspended particulate matter samples collected in February 2012 along a transect in the Rhône River plume.

Illustration 2: Abiotic degradation of terrestrial higher plant material discharged by rivers in Arctic, temperate and tropical zones.

***Future of the project**: As a following of the MORTIMER project, we intend to study the behavior of TPOM carried by atmospheric transport (in particular Saharian inputs) in seawater. On the basis of all the results obtained, a model of degradation of TPOM in the ocean (which could not be developed during the MORTIMER program due to time limitation) could be proposed.*

***Publications resulting from this project and where LEFE-Cyber is acknowledged**:*

1- Galeron M-A., Amiraux R., Charriere B., Radakovitch O., Raimbault P., Garcia N., Lagadec V., Vaultier F. et Rontani J-F. (2015) Source and behavior of particulate organic matter in the Rhône River: a lipid approach. Biogeosciences 12: 1431-1446.

2- Galeron M-A., Volkman J.K. et Rontani J-F. (2016) Degradation products of betulin: new tracers for abiotic degradation of higher plant material in the environment. Org. Geochem. 91: 31-42.

3- Galeron M-A., Vaultier F. et Rontani J-F. (2016) Oxidation products of α- and β-amyrins: potential tracers of abiotic degradation of vascular plant organic matter in aquatic environments. Environ. Chem. doi.org/10.1071/EN15237.

4- Rontani J-F. et Galeron M-A. (2016) Autoxidation of chlorophyll phytyl side-chain in senescent phototrophic organisms: a potential source of isophytol in the environment. Org. Geochem. 97: 37-40.

5- Rontani J-F., Galeron M-A. et Aubert C. (2016) EIMS Fragmentation and MRM quantification of TMS derivatives of cucurbic acid and its 6,7-stereoisomers. Rapid Commun. Mass Spectrom. 30: 2253-2264.

6- Galeron M-A., Radakovitch O., Charriere B. et Rontani J-F. (2016) Metal ions and hydroperoxide content: main drivers of lipid autoxidation in river suspended particulate matter and higher plant debris? Journal Mar. Sci. Eng. doi. 10.3390/jmse4030050.

7- Rontani J-F., Galeron M-A., Amiraux R., Artigue L. et Belt S.T. (2017) Use of di- and triterpenoid lipid tracers to confirm the significant role played by autoxidation in the degradation of terrestrial vascular plant material in the Canadian Arctic. Org. Geochem. 108: 43-50.

8- Galeron M-A., Radakovitch O., Charriere B., Vaultier F. et Rontani J-F. (2017) Impacts of coastal degradative processes: autoxidation a major player in the fate of terrestrial particulate organic matter in seawater. JGR-Biogeosciences 122: 1203-1215.

9- Galeron M-A., Radakovitch O., Charriere B., Vaultier F., Volkman J.K., Bianchi T.S., Ward N.T., Medeiros P., Sawakuchi H., Tank S., Kerhervé P. et Rontani J-F. (2018) Lipoxygenase-induced autoxidative degradation of terrestrial particulate organic matter in estuaries: a widespread process enhanced at high and low latitudes. Org. Geochem. 115: 78-92.

10- Bonin P., Prime A-H., Galeron M-A., Guasco S. et Rontani J-F. (2019) Enhancement of biotic degradation of terrestrial particulate organic matter in an estuarine salinity gradient: Interactive effects of organic matter pools and changes of bacterial communities. Aquatic Microbiol. Ecol. (Sous presse).

Thesis (Funded by Labex OT-Med):

1- Galeron M-A. Degradation of terrestrial particulate OM discharged by rivers in the Mediterranean Sea: Processes, interactions and global impacts. PhD, 20 September 2016 at Aix-Marseille University.

Communications *resulting from this project and where LEFE-Cyber is acknowledged*:

1- Galeron, M-A., Amiraux, R., Charriere, B., Radakovitch, O., Raimbault, P., Garcia, N., Lagadec, V., Vaultier, F. et Rontani, J-F., Determining the origin and fate of particulate plant-derived organic matter in the Rhone River (France): a lipid tracer review. American Geophysical Union Fall Meeting, San Francisco, CA. 16/12/2014.

2- Galeron M-A., Volkman J.K. et Rontani J-F. Using betulin as a biogeochemical tracer? Oxidation products of betulin: new tracers of abiotic degradation of higher plant material in the environment. 27th Meeting of Organic Geochemistry, Prague, 13-18 Septembre 2015.