Geophysical Research Abstracts,
Vol. 11, EGU2009-10726, 2009
EGU General Assembly 2009

Changes in fluorescence properties of dissolved organic matter during mixing processes of waters in transitional and coastal environments.

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Transitional and coastal environments represent complex systems submitted to high tidal conditions, intensive exchange and mixing between fresh water inputs and seawater. The aim of this work was to apply fluorescence spectroscopy for the study of different aquatic environments in order to investigate the evolution of fluorescent dissolved organic matter (DOM) properties during water masses mixing. Samples from various environments (aquatic ecosystems such as rivers, seawaters, coastal lagoon and estuaries) were studied. We report on the study of the three-dimensional excitation-emission matrix (EEM) fluorescence spectra of different natural water samples as well as artificial solutions prepared in laboratory under varying conditions.
EEM fluorescence spectra were recorded using a Fluorolog FL3-22 SPEX – JOBIN YVON fluorometer. In order to discuss the results of the fluorescence analysis of the different samples, we considered, on the one hand, the ratios of the intensities of the main fluorescence bands. On the other hand, fluorescence indices were calculated and discussed (HIX -humification index, and BIX - biological autochthonous input index).
Water samples were collected from the water column (surface and deep samples) during several cruises in the Gironde estuary (South Western France) from June 2001 to September 2006 (French National Program: LITEAU – GIS ECOBAG), in the Seine estuary (North Western France, French National Program: SEINE AVAL 2) from January 2001 to September 2004, in the Loire estuary (North Western France) in February 2002 and September 2004 and in the Arcachon Bay and the Leyre River, a small river flowing into the Bay (South Western France – 1998 and 2008). Artificial samples prepared with a synthetic salinity gradient were also studied in order to investigate the effects of salinity and pH on DOM fluorescence.
Marine water samples were collected in the Atlantic Ocean (surface and deep waters) during the POSEIDON-255 Cruise in 1999 from Bremerhaven in Germany to Halifax in Canada. Mediterranean coastal waters were collected from the Bay of Balaguier in Toulon (South Eastern France, MONALISA Research Group and French National Program: ECODYN) in June and October 2004, September 2005 and May 2006.
EEM spectra of natural samples collected from the Arcachon Bay and artificial samples were compared. The artificial salinity gradient was obtained by dilution of a freshwater sample (from the Leyre River flowing into the Bay, S=0) with synthetic seawater (ultrapure water + salts - S=36).
Spatial and temporal variations of DOM fluorescence properties were observed in the Gironde, Loire and Seine estuaries depending on environmental conditions (salinity, maximum turbidity zone (MTZ)). We observed seasonal effects and different trends in composition as well as in behaviour or production of DOM. Very different results were obtained for the Atlantic water samples giving us a typical signature for marine waters. Similar HIX values were obtained for Mediterranean coastal waters.
Seasonal variations of DOM were observed in the Seine estuary where higher contents of humified DOM and dissolved organic carbon (DOC) were found during the winter season while fluorescent biological organic material was produced upstream and downstream of the MTZ during the summer.
Humic-like substances represented the major fraction of DOM in the very turbid Gironde estuary although biological production was very high for salinities higher than 25 all year long. Seasonal variations of the HIX parameter were observed with lower values in winter and the highest one obtained in summer.
The HIX maxima were determined in the Loire estuary and in the Gironde MTZ. We can then conclude that the DOM was more humified in this particular zone of the Gironde estuary. The seasonal variation of BIX along this estuary was less significant than for HIX. However the highest values were obtained in summer.
The marine waters (Salinity>30) were characterized by similar values of this parameter independently of the

season.

Salinity and pH effects on DOM fluorescence were investigated. Salinity itself appears to have no detectable effect on the fluorescence signature of DOM. pH manifests considerable effects that are probably due to speciation of the organic matter and changes of conformation of this macromolecular material. Nevertheless these modifications are negligible for the studied samples (pH range: 7-8).

This work showed that the use of fluorescence indices, intensity ratios, HIX and BIX parameters, was particularly well adapted to the characterisation of DOM in marine and coastal environments. The number of samples studied from different environments (freshwaters to pure marine waters, under various conditions) allowed us to draw up a scale of values for each index. These new criteria for the characterisation of DOM in aquatic environments will be very useful and can be proposed as an easy way to define DOM characteristics in such ecosystems.