Introduction

The "DYNAMIT " project was set up to study the agricultural impact on the biogeochemical cycling of organic matter (OM) in natural waters and its fate in the freshwater - seawater mixing zone. Three main reasons are behind this choice: (i) agricultural activities are obviously a major threat to human water security and biodiversity, (ii) the composition of the organic matter is still poorly characterized and (iii) its behavior in the coastal aquatic system is far from being understood.

DYNAMITE focuses on Brittany since this is the first agricultural region in France, the largest agricultural exporter countries of the world and the second leading agricultural power of the European Union. In 2006, after several years of green tides and heavy economic losses, the Brittany region was classified in Europe as an area sensitive to eutrophication and has recently been mapped as one of the world regions with the greater threat to human water security and biodiversity (Fig.1).

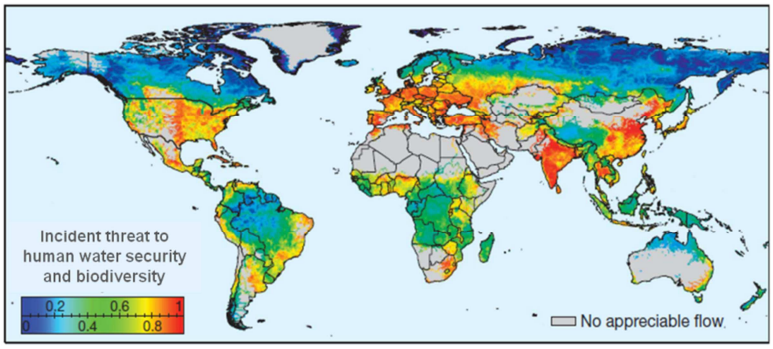

Figure 1. Brittany (France), one of the regions with the highest incident threat to human water security and biodiversity. Colour spectra depict measures of threat, increasing from blue to red. **(Vörösmarty et al., 2010)**

One of the difficulties encountered in the consideration of OM in aquatic environments concerns the terminology, given the large number of different names and acronyms used [9]. In fact, this diversity merely reflects the variety of approaches applied to the study of OM, leading to the definition and measurement of different operationally-defined fractions. The term 'organic matter' is widely used to refer to all hydrocarbon compounds, other than living organisms, occurring naturally and from human activities. The Dissolved OM (DOM) is generally operationally distinguished from the Particulate OM (POM) through a 0.45 µm filtration. Because of the diversity of processes of synthesis and degradation, the number of constituents in the DOM mixture can be considered to be infinite **(Huber et al., 2011).** Despite more than 40 years of research on DOM, its composition is still poorly characterized due to 2 main reasons: first the complex mixtures of compounds exhibit a strong heterogeneity at any level and second methods able to account for OM complexity are sorely needed **(Filella, 2008)**. Indeed, research on DOM have nearly always been addressed by sum parameters like DOC, UV absorption, or fluorescence which could offer the advantage to be more or less representative of the sample but poorly characterize the composition of DOM. Therefore, the first objective of this project and its originality is to analyze for the first time the entire DOM in coastal and estuarine waters through the transfer and development of recent advances of two analytical techniques; one chromatographic (LC OCD- OND) and the other electrochemical (DP -AdCSV). In a more general way, “Dynamite” project was set up: (1) to characterize the fine composition of riverine and estuarine DOM considering the whole DOM, (2) to quantify the spatial and temporal release of OM from agricultural activities and relate the DOM changes to specific land-use and (3) to determine the dynamics of OM through temperate estuaries under strong agricultural activities and quantify the flux of OM and organic nitrogen from the river to the ocean.

Work performed in the first year

Complying with the targets set in the program (PartB – page 20), we first conducted a series of 37 sampling campaigns (12-month monitoring in 2014) on 4 rivers in Brittany (Saint Rivoal, Aulne Yar and Pénze), chosen by the nature of their watershed and the more or less marked agricultural impact. In the

case of the Aulne River, estuarine waters were collected monthly from December 2013 to December 2014. To cover the whole salinity gradient, sampling stations were selected according to their salinity (Ssurface ≈ 0, 3, 6, 9, 12, 15, 18, 21, 24, 28, 30 and 34). Then, analysis of different families of organic compounds was performed by LC-OCD-OND and an already existing electrochemical technique in the laboratory (DP-CSV). Two scientific papers were made; one of this is published (**Marie et al., 2015**) and the other is under review. The most significant results are presented below. This first step was made concurrently with the acquisition and the startup to a liquid chromatography coupled to organic carbon, organic nitrogen and UV detector (LC-OCD-OND). In addition to the permanent staff of the laboratory, a PhD student, and a student in Master degree participated in the field work and in the analysis

Main results

The Penzé River (NW Brittany, France), was sampled during one hydrological year from 05/01/2012 to 09/01/2013 with an 8 day frequency at Prat Guen (3°54'42.5" W–48°31'18.8"N) 1 km from the village of Saint Thégonnec, outside the turbid area and upstream of the salty zone of the estuary. We have examined the dynamics and sources of reduced sulfur, HS and DOC in this river system affected by agricultural practices. New differential pulse cathodic stripping voltammetry method (DP-AdCSV; Pernet-Coudrier et al., 2013) was successfully applied to measure glutathione-like compounds (GSHs), thioacetamide-like compounds (TAs) and a liquid chromatography coupled to organic detector (LC-OCD-OND) to analyze HS and DOC at high frequency. The streamflow-concentration patterns, principal components analysis and flux analysis allowed discrimination of the source of each organic compound type. Surprisingly, the two RSS and HS detected in all samples, displayed different behavior. As previously shown, manuring practice is the main source of DOC and HS in this watershed where agricultural activity is predominant. The HS were then transferred to the river systems via runoff, particularly during the spring and autumn floods, which are responsible of >60% of the annual flux. TAs had a clear groundwater source and may be formed underground, whereas GSHs displayed two sources: one aquagenic in spring and summer probably linked to the primary productivity and a second, which may be related to bacterial degradation. High sampling frequency allowed a more accurate assessment of the flux values which were 280 tC y^{-1} for DOC representing 20 kgC ha^{-1} y^{-1}. HS, TAs and GSHs fluxes represented 60, 13, and 4% of the total annual DOC export, respectively.

The humic substances diagram **(Huber et al., 2011)**, i.e. plotting the aromaticity versus the molecularity of humic substances, can provide information about the HS origin. The HS data from the Penzé River were found in the upper center of the diagram (red dots, Fig. 2).

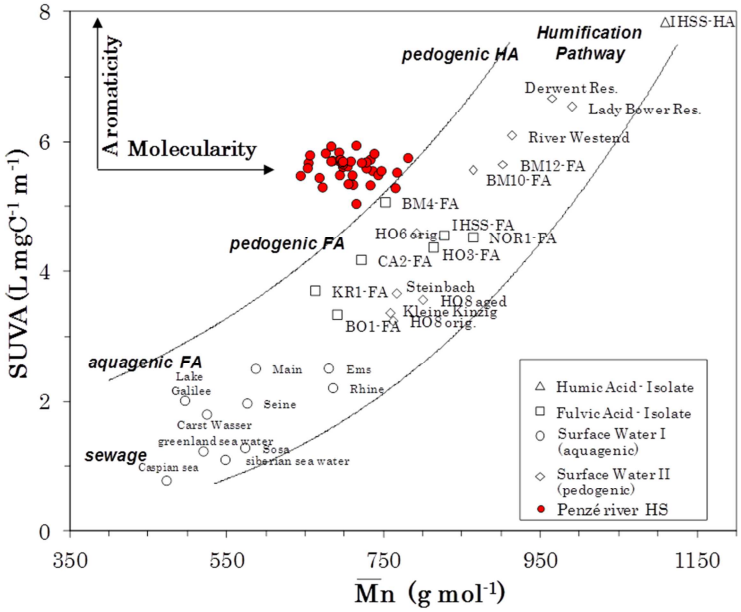

Fig.2. The specific UV absorbance (SUVA, i.e. aromaticity) of HS from the Penzé River is plotted against the nominal average molecular weights, shortly expressed as molecularity. Other data points come from Huber et al. (2011).

Therefore these HS are clearly of pedogenic origin between FA and HA. This area reflects small rivers and creeks whose HS originate from areas where the high hydraulic energy allows relatively high molecular weight FA from soils to be washed into the water body **(Huber et al., 2011)**. Often the aromaticity of these FA is low due to sunlight induced bleaching of HS in the photic zone **(Huber et al., 2011)**. However, the HS from the Penzé River do not displayed low SUVA, i.e. sunlight induced bleaching of HS is negligible probably for the same reasons previously explained (high flow velocity and the shadowed river bank). The hallmarks of the Penzé HS are the very low molecular weights, 700 g mol−1 against 900 g mol−1 for HS with similar SUVA. Extensive agricultural activities (cattle, pig and poultry) are taking place on the Penzé catchment resulting in manure spreading throughout the year as organic fertilization **(Waeles et al., 2013)**. Besides, it has been shown that high molecularweights (MW) frommanure-derived organic matter (cattle, pig and poultry) were preferentially sorbed on soil whereas low MW were leached (**Aoyama and Kumakura, 2001; Ohno et al., 2007)**. This feature is thus highlighting the origin of the Penzé HS, i.e. manure and pedogenic.

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