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Inventory of sedimentary organic matter in modern wetland (Marais Vernier, Normandy, France) as source-indicative tools to study Holocene alluvial deposits (Lower Seine Valley, France)

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**Keywords**: Wetland deposits; Organic matter; Palynofacies; Optical markers; Palaeoenvironment; Holocene

### **Abstract**

Palynofacies' analysis was developed for petroleum exploration, but it is now commonly used to differentiate the major constituents of the sedimentary organic matter (SOM) in Postglacial deposits. Our work aimed at studying the SOM distribution in a present wetland of the Seine estuary (Vernier Marsh) in order to provide comparative elements to interpret the composition of SOM in the Lower Seine Valley alluvial infilling. In the Vernier Marsh, the distribution of major constituents is heterogeneous. Thus, for each depositional environment studied (soils, drainage ditches, channels, ponds), the composition of SOM has been characterized by using two ternary diagrams ("Amorphous OM/Preserved Phytoclasts/Transformed Phytoclasts" and "Opaque/Amorphous/Gelified Particles"; OP/AP/GP). This approach allowed us to define four optical indices that can be used to estimate the relative abundances of principal organic fractions in mixed deposits based on the origin of SOM (aquatic/terrestrial), its source areas (vegetation, soils, river), and controls of early diagenetic changes (aerobic/anaerobic conditions, advanced oxidation). "Amorphous OM contents" increase from terrestrial environments to fluvial deposits and evaluate the abundance of planktonic contribution. "Preserved / transformed phytoclasts ratio" decreases from sites of production to those of deposition indicating the degree of degradation of terrestrial materials. "OP contents" allow one to define fluvial (high values) and palustrine (low values) environments. "GP / AP ratio" allows one to discern soil (low values) and plant (high values) supplied areas. Finally, these optical compositional indices are measured in Holocene deposits and used to complete palaeoenvironmental reconstructions.

#### 1. Introduction

Wetlands are among the most important ecosystems that include specific biotopes (Whigham, 1999). In addition, they are favourable for organic matter (OM) preservation and for peat accumulation (Clymo, 1983). The latter is the subject of numerous works aiming to understand the possible influence of human activities on natural environments (Barber et al., 2003) and the function of the global carbon cycle (Gorham, 1991 and Malmer, 1992). The study of sedimentary OM is also the subject of a considerable amount of work done through geochemical analyses. In order to trace the origin, transport and fate of organic matter from diverse sources, isotopic and/or molecular marker (biomarker) analyses have been applied. Although each method has are limitations. For auite successful, there example. characterization of natural and anthropogenic OM by bulk chemical methods provides an averaged signal which can be difficult to interpret because of its heterogeneous nature. However, a large part of this heterogeneity appears at the micrometer or nanometer scale (Tyson, 1995). So, the micromorphological characterization of OM constitutes a useful and complementary method for determining the nature of OM and its origin, and for understanding its diagenetic evolution (Laggoun-Défarge et al., 1995 and Cohen et al., 1999). One mean of analysing OM, palynofacies' analysis, has classically been used to determine the petrographic composition of particulate OM (<u>Tyson</u>, 1995). The purposes of the current work were to (1) study the spatial distribution of the principal sources of organic matter in a present-day wetland (i.e. Vernier Marsh), (2) define the optical markers of both the sources and depositional environments of OM and (3) use these markers to reconstruct paleoenvironments of Holocene fluvio-palustrine deposits (i.e. Seine Valley filling).

# 2. Area descriptions and material studied

## 2.1. Site description

The Vernier Marsh, located in an abandoned meander of the Seine River (France, 49°25′ N, 0°27′ E), is the largest remaining wetland system in the region (about 4500 ha; Fig. 1). The bedrock is Upper Cretaceous chalk and the surface of the marsh ranges between altitudes of 2 or 3 m above sea level. The northern part harbours an alluvial marsh and a polder, while the southern part shelters a peaty marsh (Fig. 1c). This peaty zone (about 1600 ha) presents a mosaic of environments, which differ according to the nature of water resources, the origin and nature of the sedimentary particle supply, and the local ecological conditions (Mesnage et al., 2002). In the southwestern part, terrestrial environments are composed of wet meadows and wooded parcels, and cultivated and grazed fields. Cattails (Typha) and reeds (Phragmites) characterize the vegetation of the wettest areas. In slightly drier wet meadows, rushes (Juncus), sedges (Carex) and various grasses

(*Poaceae*) are dominant. The hills surrounding the marsh on three sides are covered by oaks (*Quercus*) and beech (*Fagus*). The eastern part of the peaty marsh is occupied by a pond (the Grand-Mare) in which both drainage ditches and foot slope springs are empty (*Fig. 1c*). The water surface covers an area of about 40 ha, with a mean depth of 0.5 m. Before 1995, this pond has been periodically fed with Seine River inputs via the Saint-Aubin Channel. A lock that is regularly opened to manage the pond water level during the dry season controls flow in the channel. Several shallow and closed pools are associated with the Grand-Mare. The two largest ones are the Crevasse pool, which collects drainage ditch water, and the Petite-Mare pool, which is isolated from the Grand-Mare pond (*Fig. 1*d).

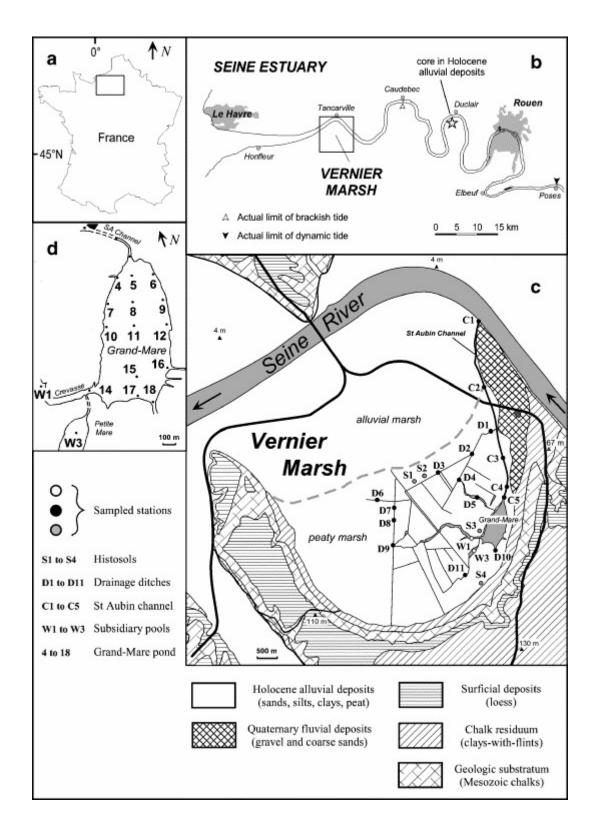


Fig. 1. Location of study site and sampling stations. (a) Location of the Lower Seine Valley in France. (b) Details of the Lower Seine Valley. (c) Simplified geomorphologic map of the Vernier Marsh and location of terrestrial, ditch and channel sampling stations. (d) Location of sampling stations in the Grand-Mare and others ponds.

#### 2.2. Sampling

Surface sediments were sampled at 40 stations in aquatic (33 stations) and terrestrial (7 stations) areas (Fig. 1; Table 1). Several environments were sampled according to their function in the depositional system (source areas, transportation systems, sites of deposition). Histosols (4 stations, 10 samples) are representative of wet terrestrial environments (Fig. 1c). On profile, two horizons were distinguished in histosols according to the abundance of fresh plant tissues, these were plant litter horizons (L) and humic layers (H). Surficial sediments in ditches (10 to 20 cm depth) were sampled at various points in the wetland (10 stations; Fig. 1c). Surficial sediments (10 to 20 cm depth) were also sampled in shallow open water environments (20 stations), as spot samples in pools and according to a more or less regular grid in the Grand-Mare (Fig. 1c). Recent alluvial deposits were sampled on the bank of the Seine River and are considered to characterize materials of fluvial origin (3 samples; not plotted). In addition, several forest profiles were sampled in the catchment area (3 stations, 8 samples; not plotted). For those, four principal horizons were distinguished according to the state of degradation of OM and the abundance of mineral materials. These horizons are identified at plant litter (L), fragmentation (F), and humic (H) layers (Table 1).

Holocene alluvial deposits constitute a representative sequence of Holocene sediments in the Seine Estuary (Fig. 1b). In the fluvial part of the Seine estuary, the sedimentary fill includes clayey and sandy loams and a thick organic sequence (4 to 6 m). These peaty deposits represent the existence of a large wetland system between 5300–5000 years BC and 1000–750 years BC. Detailed sedimentological and paleobiological studies have already been carried out on the core; sixty-three samples were studied using palynofacies' analysis (Sebag, 2002).

## 3. Palynofacies analysis

Palynofacies' analysis consists of optical analysis of organic materials that have been isolated and concentrated from carbonate and silicate phases of the sediment (i.e. kerogen, in Combaz, 1964). The digestion of mineral materials consists of hydrochloric (36%, 30 min) and hydrofluoric (40%, 45 min) attacks. These treatments lead to the loss of some organic compounds, but previous works have shown that this acid-soluble fraction represents less than 5% of total OM in geological formations and recent sedimentary deposits, and less than 10% of the soil OM (in Di Giovanni et al., 1999a and Di Giovanni et al., 1999b). Often performed in conjunction with bulk geochemical analyses (Meyers, 1997), it is a means of determining the identity and quantity of various organic sedimentary constituents (Tyson, 1995).

Table 1. : Palynofacies analysis and optical indices of surficial wetland deposits and soil profiles

Sample	es		Parti abu			org , roui	anic ndec		matt	er	(rela	tive	Opti	cal indice	es	
Locat ion	Ind ex	Typ e	A O M (%	C M ( % )	TL C ( % )	AL C ( % )	A P ( % )	G P ( % )	O P ( % )	M YC (% )	ZO O (% )	S P ( % )	A O M (% )*	Preserv ed/ transfor med	Gelifie d/ amorp hous	O P (% )*
Chal k plate au	L	Fore st soil (L)	5	1 0	1 5	20	2 0	1 0	5	15	0	< 5	5	1.26	0.41	7
	F	Fore st soil (F)	10	1 0	< 5	10	2 5	1 0	5	15	0	0	12	0.55	0.37	7
	Н	Fore st soil (H)	15	5	tr.	10	2 5	1 0	1 0	5	0	0	16	0.41	0.46	11
	L	Fore st soil (L)	tr.	1 0	2 0	30	2 0	1 5	5	5	0	0	1	1.29	0.62	7
	F	Fore st soil (F)	10	5	1 0	15	2 5	1 5	5	15	0	tr.	8	0.68	0.50	5
Seine valle y	L	Fore st soil (L)	tr.	2 5	1 5	20	5	2 0	< 5	15	0	tr.	1	2.15	3.80	3
	F	Fore st soil (F)	tr.	1 5	5	15	1 5	2 5	5	15	tr.	tr.	1	0.77	1.47	5
	Н	Fore st soil (H)	< 5	1 0	< 5	10	3 5	1 5	1 0	15	0	< 5	2	0.42	0.45	11
Peat y mars h	S1 (L)	Histo sol (5 cm)	10	5	5	15	3 5	2 0	5	tr.	0	5	11	0.43	0.59	4

Sample	es			icula ndar		org , roui	anic ndec		matt	er	(rela	tive	Opti	ical indice	es	
Locat ion	Ind ex	Тур е	A O M (% )	C M ( % )	TL C ( % )	AL C ( % )	A P ( % )	G P ( % )	O P ( % )	M YC (% )	ZO O (% )	S P ( % )	A O M (% )*	Preserv ed/ transfor med	Gelifie d/ amorp hous	O P (% )*
	S1 (H)	Histo sol (10 cm)	15	5	5	10	3 5	2 3	5	5	0	0	14	0.26	0.66	7
	S2 (L)	Histo sol (5 cm)	15	5	5	5	3 0	2 0	1 0	15	0	tr.	13	0.29	0.67	11
	S2 (H)	Histo sol (10 cm)	15	5	5	5	3	2 0	2 0	5	0	tr.	16	0.24	0.67	18
	S3 (L)	Histo sol (5 cm)	tr.	5	5	5	3	1 5	5	tr.	0	tr.	1	0.18	0.26	4
	S3 (H)	Histo sol (10 cm)	10	tr.	tr.	5	4 5	2 5	5	tr.	0	tr.	10	0.13	0.53	5
	S3 (H)	Histo sol (15 cm)	15	5	< 5	5	3 5	2 5	1 0	< 5	0	0	15	0.22	0.79	8
	S4 (L)	Histo sol (5 cm)	10	< 5	5	10	4 0	1 5	5	5	0	tr.	10	0.33	0.28	6
	S4 (H)	Histo sol (10 cm)	10	< 5	5	5	3 0	3 0	1 0	tr.	0	tr.	11	0.18	0.97	12
	S4 (H)	Histo sol (15 cm)	15	< 5	tr.	5	3 5	2 5	1 5	< 5	0	0	15	0.12	0.69	14
Saint- Aubi n	C0 1	Surfi cial dep	30	5	5	5	5	1 0	3	tr.	0	< 5	32	0.29	1.71	30

Sample	es			icula ndaı		org , roui	anic ndec		matt	er	(rela	tive	Opti	ical indice	es	
Locat ion	Ind ex	Typ e	A O M (% )	C M ( % )	TL C ( % )	AL C ( % )	A P ( % )	G P ( % )	O P ( % )	M YC (% )	ZO O (% )	S P ( %	A O M (% )*	Preserv ed/ transfor med	Gelifie d/ amorp hous	O P (% )*
Chan nel		osit														
	C0 2	Surfi cial dep osit	45	< 5	5	5	5	1 0	3 0	tr.	tr.	tr.	46	0.30	1.40	28
	C0 3	Surfi cial dep osit	35	1 0	tr.	5	1 0	1 0	2 5	tr.	0	tr.	35	0.41	0.67	24
	C0 4	Surfi cial dep osit	40	< 5	5	5	5	tr.	3 5	tr.	tr.	tr.	41	0.33	0.29	33
Ditch es	D0 1	Surfi cial dep osit	25	< 5	5	5	2 0	1 5	2 0	< 5	1	1	27	0.33	0.74	18
	D0 2	Surfi cial dep osit	30	5	< 5	5	1 5	1 0	2 5	5	tr.	< 5	29	0.27	0.92	23
	D0 3	Surfi cial dep osit	20	5	5	5	2 0	2 0	1 5	< 5	tr.	2	22	0.30	0.82	16
	D0 4	Surfi cial dep osit	30	5	< 5	5	2 0	1 5	1 0	2	tr.	< 5	32	0.32	0.64	11
	D0 5	Surfi cial dep osit	15	5	0. 5	10	4 5	1	1 0	2	tr.	< 5	15	0.25	0.20	9
	D0 7	Surfi cial dep osit	20	5	5	10	3 5	1 0	1 0	1	0	< 5	20	0.31	0.33	10

Sample	es		Parti abu			org , roui	anic ndec		matt	er	(rela	tive	Opti	ical indice	es	
Locat ion	Ind ex	Тур е	A O M (%	C M ( % )	TL C ( % )	AL C ( % )	A P ( % )	G P ( % )	O P ( % )	M YC (% )	ZO O (% )	S P ( %	A O M (% )*	Preserv ed/ transfor med	Gelifie d/ amorp hous	O P (% )*
	D0 9	Surfi cial dep osit	< 5	1 0	< 5	15	3 5	1 5	1 5	< 5	0	< 5	4	0.42	0.40	13
	D1 0	Surfi cial dep osit	20	5	< 5	10	2 5	1 5	1 5	<5	tr.	tr.	20	0.40	0.54	13
	D1 1	Surfi cial dep osit	5	1 0	5	10	3 0	2	1 0	5	0	1	7	0.42	0.73	8
Gran d- Mare	GM 04	Surfi cial dep osit	30	5	5	15	1 5	1 5	1 0	< 5	0	tr.	28	0.66	1.13	9
	GM 05	Surfi cial dep osit	15	5	5	10	2	2 5	1 5	tr.	tr.	tr.	17	0.32	1.14	15
	GM 06	Surfi cial dep osit	20	1 0	1	10	1 5	1 5	1 5	tr.	tr.	tr.	19	0.60	0.94	15
	GM 07	Surfi cial dep osit	30	1 0	5	10	1 5	1 0	1 0	tr.	tr.	tr.	29	0.69	0.69	12
	GM 08	Surfi cial dep osit	35	tr.	< 5	10	1 5	2 0	1 5	tr.	0	tr.	35	0.32	1.36	14
	GM 09	Surfi cial dep osit	15	5	1 0	15	2 0	1 5	1 5	tr.	0	tr.	15	0.61	0.75	16
	GM 10	Surfi cial dep	30	1 0	5	10	1 0	2 0	1 0	tr.	tr.	< 5	29	0.55	2.44	11

Sample	es			icula ndaı		org , roui	anic ndec		matt	er	(rela	tive	Opt	ical indice	es	
Locat ion	Ind ex	Тур е	A O M (% )	C M ( % )	TL C ( % )	AL C ( % )	A P ( % )	G P ( % )	O P ( % )	M YC (% )	ZO O (% )	S P ( % )	A O M (% )*	Preserv ed/ transfor med	Gelifie d/ amorp hous	O P (% )*
		osit														
	GM 11	Surfi cial dep osit	40	< 5	< 5	5	5	2 0	1 5	tr.	0	tr.	42	0.35	4.40	13
	GM 12	Surfi cial dep osit	15	1 0	5	15	2 0	2 0	1 0	tr.	tr.	tr.	14	0.69	1.17	9
	GM 14	Surfi cial dep osit	25	5	tr.	5	1 0	3 0	1 5	tr.	< 5	tr.	27	0.26	2.90	14
	GM 15	Surfi cial dep osit	30	5	5	15	1 0	2 0	1 0	tr.	< 5	tr.	29	0.55	2.20	10
	GM 16	Surfi cial dep osit	30	1 0	5	10	1 0	2 0	1 5	< 5	tr.	tr.	29	0.49	2.00	13
	GM 17	Surfi cial dep osit	20	1 5	1 0	15	1 0	2 0	1 0	< 5	tr.	tr.	22	0.89	2.00	8
	GM 18	Surfi cial dep osit	25	5	5	10	5	3 0	1 0	tr.	tr.	tr.	27	0.53	4.14	9
Crev asse	W1	Surfi cial dep osit	15	5	5	15	1 5	3 0	1 0	tr.	tr.	tr.	17	0.41	1.76	9
Petite - Mare	W3	Surfi cial dep osit	20	5	< 5	15	1 5	3 0	1 0	< 5	0	0	20	0.38	2.00	8

(\*): results obtained by counting. AOM: amorphous organic matter; CM: cuticles; TLC: transparent ligno-cellulosic fragments; ALC: altered ligno-cellulosic fragments; AP: amorphous particles; GP: gelified particles; OP: opaque particles; MYC: mycelium; ZOO: zooclasts; SP: spores and pollen.

This approach has been classically used to study marine geological formations, as it allows one to estimate the petroleum potential of a rock, to determine biostratigraphic correlations, to identify the principal sources of OM, and to reconstruct the evolution of depositional environments (<u>Batten, 1996</u> and <u>Tyson, 1995</u>). In continental deposits, palynofacies' analysis allows one to identify and distinguish the results of lacustrine (<u>Di Giovanni et al., 2000</u>) and palustrine processes (<u>Laggoun-Défarge et al., 1999</u>). It may also be used to study the effects of synsedimentary processes and early diagenetic changes in peatland deposits (<u>Bourdon et al., 2000</u>) or the incorporation of OM into soils (<u>Di Giovanni et al., 1999c</u>).

In palynofacies' preparations, several categories of particulate OM can be distinguished according to their optical properties: there include amorphous OM, discrete elements, and phytoclasts (<u>Fig. 2</u>a; <u>Batten, 1996</u> and <u>Tyson, 1995</u>). In addition to these organic constituents, opaque mineral particles (e.g. sulphides, oxides) often appear in residues.

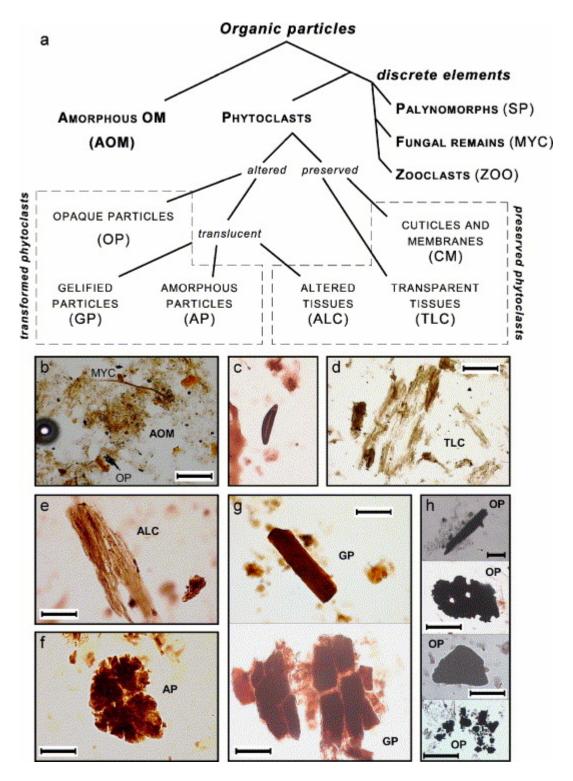


Fig. 2. (a) Simplified classification of the OM observed in transmitted optical microscope (modified from  $\overline{\text{Tyson}}$ , 1995). Morphological criteria allow us to distinguish three main categories: AOM (diffuse outlines), discrete elements (recognizable organisms or organs) and phytoclasts (resulting from degradation of the plant fragments). Phytoclasts are divided into several classes according to their nature and to their degree of degradation (preserved phytoclasts) or to characters acquired during their degradation (transformed phytoclasts), (b) amorphous organic matter (AOM), (c) discrete elements (diatom), (d) ligno-cellulosic transparent fragments (TLC), (e) reddish altered phytoclast (ALC), (f) reddish amorphous particle (AP), (g) gelified particles (GP), (h) various opaque particles (OP), scale bar: about 10  $\mu$ m.

#### 3.1. Amorphous OM

As seen in optical microscope (transmitted light), amorphous OM (AOM) consist of particles that are flaky, lumpy, or granular, and that have indistinct outlines. They are also typically of variable size, degree of opacity and color (<u>Fig. 2</u>b). AOM retains various optical, chemical and structural properties that originate as bacterial, algal or planktonic matter (<u>Tyson, 1995</u>).

#### 3.2. Discrete elements

Discrete elements are recognizable organs or organisms (<u>Fig. 2</u>c). They are classified according to their taxonomic level and/or to their morphotype, these include palynomorphs (spores and pollens), fungal remains (mycelium fragments) and zooclasts (chitinous fragments of arthropods).

#### 3.3. Phytoclasts

Phytoclasts represent whole particulate constituents produced by higher plants or derived from their degradation (Fig. 2d-h). Two categories of phytoclasts were distinguished in this study: preserved phytoclasts (CM, TLC, ALC) in which initial biological structures are preserved, and transformed phytoclasts (AP, GP, OP) that are characterized by acquired degradation properties. These acquired optical properties (shape, texture, opacity) depend essentially on the nature and conditions of their degradation or thermal maturation (Batten, 1996 and Tyson, 1995).

## 3.3.1. Preserved phytoclasts

Cuticles and membranes (CM) present a fine pellicular shape and are generally of large size (>  $100 \mu m$ ). Ligno-cellulosic fragments are observed in various degradation stages. The transluscent fragments (TLC) present well-preserved biological internal structures (<u>Fig. 2</u>d). Reddish altered fragments (ALC) present dull or indistinct outlines, reddish color and more or less altered internal structures (<u>Fig. 2</u>e).

## 3.3.2. Transformed phytoclasts

Reddish amorphous particles (AP) appear as reddish flakes with diffuse but recognizable outlines that, sometimes, have residual internal structures (Fig. 2f). Gelified particles (GP) present a homogeneous texture, variable color (brown to amber), true outlines, and commonly angular shape but, sometimes, dulled angles (Fig. 2g). Opaque particles (OP) include various constituents which are not easily distinguished in transmitted light: the main optical criteria used to distinguish them are general shape, outline aspects and possible residual botanical structures (Fig. 2h).

The quantitative palynofacies' composition is determined by counting particles, as they are seen in the microscope. The use of an objective with a reticule network allows the viewer to assign a value to each particle that is proportional to its apparent surface area. The results are, thus, expressed as relative areal percentages that are rounded to the closest 5%. To guarantee measurement reproducibility, we analysed each slide until (1) at least 15 optical areas have been studied and 300 particles were counted in order to consider the distribution of particles on the slide, and (2) the variations of relative abundances among the last five areas were lower than 5% in order to reduce the influence of the largest particles.

#### 4. Results

#### 4.1. Quantitative composition

The average composition of the samples was determined from the relative abundance of the principal organic constituents (Fig. 3). Compositions consisted, on average, of 70% phytoclasts and 25% AOM. The discrete elements (MYC, ZOO, SP) represent less than 5% of any samples. Table 1 presents the compositional assemblages of samples collected in the different parts of the depositional system, including forest soils (L, F, H) and histosols (S), channel deposits (C1 to C4), ditches (D1 to D11), ponds (GM4 to GM18) and pools (W1 to W3).

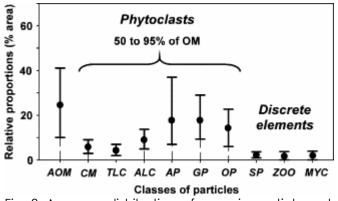


Fig. 3. Average distribution of organic particles established by palynofacies' analysis (relative areas). AOM: amorphous organic matter; CM: cuticles; TLC: transparent ligno-cellulosic fragments; ALC: altered ligno-cellulosic fragments; AP: amorphous particles; GP: gelified particles; OP: opaque particles; SP: spores and pollen; ZOO: zooclasts; MYC: mycelium.

Phytoclasts are dominant in soils (range of 75% to 90% in L horizons) and minimal in channel deposits (range of 30% to 65% in C samples; <u>Table 1</u>). The well-preserved phytoclasts (CM, TLC, ALC) represent generally less than 30% (except in the plant litters and some subquaeous deposits; <u>Table 1</u>), whereas transformed phytoclasts (AP, GP and OP) range from 35% to 60% of the OM. These latter are composed, on average, of 17% amorphous particles (AP), 16% gelified particles (GP), and 14% opaque particles (OP). The amorphous OM (AOM) contents vary according to the sampled stations: they are less

than 15% in soils, between 15% and 30% in the majority of drainage ditches, more than 15% in ponds, and more than 30% in Saint-Aubin Channel (<u>Table 1</u>). In addition, slight variations of AOM contents were measured for some stations. The sedimentary OM of modern marsh deposits includes four main fractions (AOM, AP, GP and OP) there together constitute a range from 60% to 90% of OM.

#### 4.2. Palynofacies and depositional environments

Quantitative composition can be used to define the palynofacies' distribution of different environments of the depositional system (Fig. 4). Terrestrial environments and drainage ditches show similar palynofacies' distributions (Fig. 4a and b). The major organic fractions are mainly AP (generally more than 30%) and GP (15% to 25%) with lesser amounts of OP and AOM (10% to 15%). However some differences occur in ditches with a relative enrichment in AOM and a relative impoverishment in AP and GP contents compared to histosols.

Open water environments (pools and ponds) show a palynofacies distribution dominated by AOM (30%; <u>Fig. 4</u>c and d). Differences between the northern and southern part of the Grand-Mare appear in phytoclast contents: AP contents are high (15%) in the northern zone (stations 4 to 10), while GP contents are high (25%) in the southern zone (stations 11 to 19). Finally AOM (40%) and OP (25%; <u>Fig. 4</u>e) dominate the palynofacies' distribution of the Saint-Aubin Channel.

Four palynofacies' distributions are defined in the depositional system based on the preceding data and observations: (1) AP are dominant in histosols and in drainage ditches; (2) AOM and GP are dominant in the southern zone of the Grand-Mare; (3) AOM, AP, and GP are dominant and OP contents are variable in the northern zone of the Grand-Mare; (4) AOM and OP are dominant in the Saint-Aubin Channel and in some pond and ditch stations.

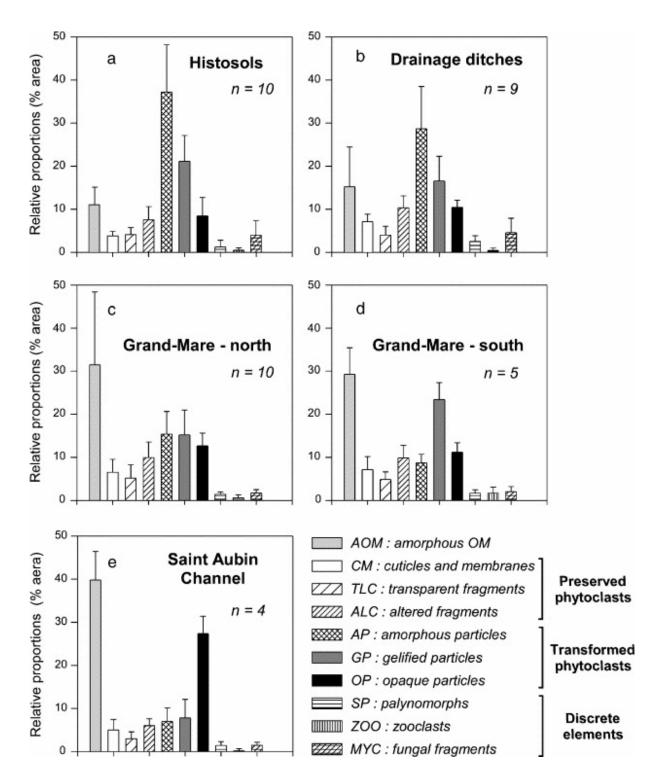


Fig. 4. Average distribution of organic particles established for each environment. The four main classes (AOM, AP, GP, OP), which are present in all environments, allow one to define four characteristic palynofacies: histosols and drainage ditches (a and b), northern (c) and southern (d) part of the Grand-Mare, and Saint-Aubin Channel (e).

#### 5. Discussion

#### 5.1. Origin of OM and degradation of the terrestrial fraction

The occurrence and composition of OM in sediments and sedimentary rocks reflect different variables, including differences in production, transport to the depositional site, and diagenetic alterations (Tyson, 1995). We have quantified various components of the sedimentary OM, and the results have been summarized in paired ternary diagrams. The first ternary diagram (lefthand diagrams, Fig. 5) depicts the relative proportions of AOM, preserved phytoclasts (CM, TLC, ALC) and transformed phytoclasts (AP, GP, OP). It is used to illustrate the origin (i.e. terrestrial or aquatic) of the principal organic particles and the state of degradation of terrestrial particles. The second ternary diagram (OP/AP/GP; right-hand diagrams, Fig. 5) relates to the early diagenesis of transformed phytoclasts. The optical properties of these particles were acquired during degradation (Batten, 1996 and Tyson, 1995). Their occurrence in all studied samples indicates, on one hand, that their genesis is not limited to a specific environment. On the other hand, these particles are not distributed uniformly in the studied palynofacies (Table 1 and Fig. 4).

#### 5.1.1. Terrestrial environments

Typical soil assemblages are dominated by transformed phytoclasts (<u>Fig. 5</u>a). The state of preservation of phytoclasts allows one to distinguish forest litter (60% to 90% preserved tissues in L and F samples) and humic horizons (50% to 80% transformed particle in S samples). This evolution with depth can be related to increasing AP contents (<u>Table 1</u>) which are a result of morphological biodegradation of plant tissues (<u>Laggoun-Défarge et al., 1999</u>). In agreement with previous work, these amorphous particles represent a pedogenetic OM that form in soils and peat (<u>Bourdon et al., 2000</u>, <u>Di Giovanni et al., 1999c</u>, <u>Lallier-Vergès et al., 1998</u> and <u>Noël et al., 2001</u>) and reworked from its terrestrial source areas (<u>Buillit et al., 1997</u>, <u>Patience et al., 1996</u> and <u>Sifeddine et al., 1996</u>).

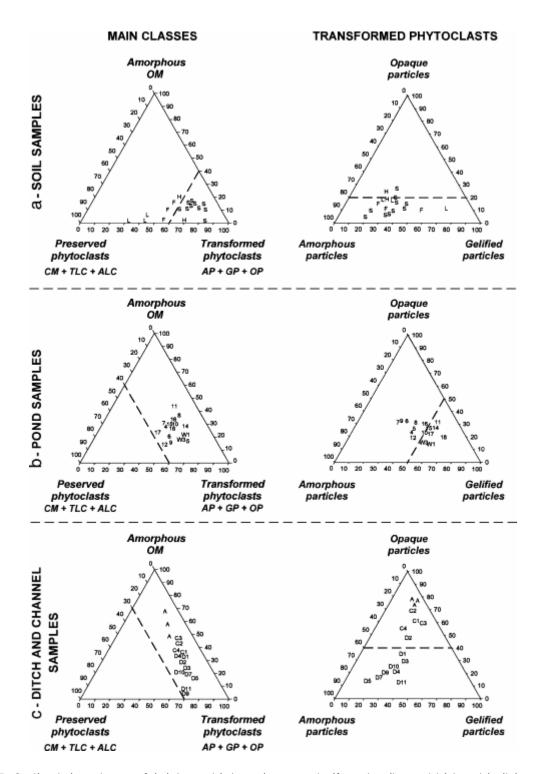


Fig. 5. Optical signatures of (a) terrestrial environments (forest soils and histosols), (b) aquatic environments (Grand-Mare pond and pools) and (c) drainage ditches and Saint-Aubin Channel. Nature of main organic constituents (AOM, preserved and transformed phytoclasts) and composition of transformed phytoclasts (amorphous, gelified or opaque particles).

#### 5.1.2. Pond and pools

In aquatic environments, OM is characterized by a large variation of AOM contents (10% to 40%). Pond samples are characterized by relatively high terrestrial plant tissues' contents (Fig. 5b). Plant fragments, which accumulate directly in aquatic environments (i.e. ponds), are less degraded than they are in aerobic environments (i.e. soils). In addition, pond environments present compositional signatures enriched in GP (20% to 30% in the southern zone of the Grand-Mare) as compared to other environments. Previous observations (Alpern, 1976, Noël et al., 2001 and Sifeddine et al., 1998) tend to relate GP formation to the degradation of plant tissues in aquatic environments (pools, ponds, lakes) or in anaerobic conditions (catotelm of peat, hydromorphic soils). However, this point is debatable because of the variety of constituents categorized as "gelified particles" and because of the variety of factors controlling the gelification process. In spite of these uncertainties, the results presented here clearly illustrate an empirical relationship between aquatic environments and a GP enriched optical signature.

#### 5.1.3. Flowing water environments

The ditch stations (D1 to D4), which receive waters from the Saint-Aubin Channel, show a relative enrichment in AOM (about 20% to 30%) compared to other stations (D5 to D11). Indeed, channel deposits (C1 to C5) present an optical signature that is even more enriched with AOM (40% to 50%) than ditch deposits. In the same way, alluvial samples (A) also bear AOMdominated assemblages (> 50%). Thus, the range of compositions illustrates an AOM gradient from terrestrial stations (histosols, S; Fig. 5a) and soil-derived samples (ditches, D; Fig. 5c) to pond (Fig. 5b), and then fluvial deposits (A and C; Fig. 5c) as a result of an increasing aquatic contribution. In flowing water environments (i.e. ditch, channel and river), the proportion of opaque particles (OP) gradually increases from drainage ditches to fluvial deposits (Fig. 5c). This change can be related to the increasing alteration of the terrestrial components during their transport (<u>Tyson</u>, <u>1995</u>). These OP contents include heterogeneous constituents which could have various origins such as combustion residues (soot and charcoal), strongly altered and oxidized phytoclasts caused by repeated cycles of degradation (black or charcoallike phytoclasts) and/or a probable fraction degraded by thermal maturation (coalified or charred material) and inherited from the geological substratum (Di Giovanni et al., 1999b, Di Giovanni et al., 2002, Batten, 1996 and Tyson, 1995). Thus, a large portion of these opaque particles may constitute an organic fraction produced outside the system, as shown by their limited abundances in the pond and terrestrial peaty marsh environments.

#### 5.2. Optical index definition

The use of relative proportions involves semi-quantitative estimations (rounded to the nearest 5%). The use of ratios allows one to overcome these inconveniences and to study the results statistically (i.e. using standard error and other statistical indices). In this study, the choice of four ratios is based on the preceding observations and interpretations that are summarized in the Table 2. The "AOM contents" are used to quantify the aquatic contribution. The "preserved phytoclasts / transformed phytoclasts ratio" allows one to quantify the degree of degradation of the terrestrial fraction. The "OP contents" increases with the oxidation of terrestrial source materials. The "GP / AP ratio" is used to discriminate sites which have material reworked from soil as opposed to sites where fresh plant debris fall directly into a basin, and decayed (Fig. 6).

Table 2. : Terms and abbreviations used in this study to describe organic particles

Abbreviation	Designation	Interpretat Seine Valle		depositional syste	ems of the Lower
		Origin	Nature	Degree of preservation	Principal sources (conditions of formation)
AOM	Amorphous organic matter	Aquatic	Planktonic	Observed in various stages of preservation according to lithology and age of deposits	No information because these particles are related to specific environments
СМ	Fragments of cuticle and membrane	Terrestrial	Phytoclasts	Resistant biological tissues generally well-preserved	Directly from vegetation, plant litters
TLC	Transparent ligno- cellulosic debris	Terrestrial	Phytoclasts	Well-preserved plant fragments in which initial biological structures are recognizable	Directly from vegetation, fresh plant litters
ALC	Altered ligno- cellulosic debris	Terrestrial	Phytoclasts	Transformed plant debris in which biological structures are observable but partially altered	Old plant litters and surficial soil layers (aerobic degradation of ligneous plant debris)
AP	Reddish amorphous particles	Terrestrial	Phytoclasts	Degraded particles without recognizable biological structures at micrometer scale	Humic soil layers, old plant litters (humification or aerobic diagenesis of ligneous plant debris)
GP	Gelified particles	Terrestrial	Phytoclasts	No information because these are particles related to specific environments	Hydromorphic soils, catotelm peat, aquatic environments (subaquatic diagenesis of plant tissues)
ОР	Dark opaque particles	Terrestrial	Phytoclasts	Very altered fragments related to	Geological substratum, fires, river

Abbreviation	Designation	Interpretat Seine Valle		depositional syste	ems of the Lower
		Origin	Nature	Degree of preservation	Principal sources (conditions of formation)
				intense or repeated processes of degradation	transport (coalification, combustion, oxidation)
SP	Spores and pollens	Aerial	Palynomorphs	Resistant biological products generally well- preserved	Local or regional vegetation
ZOO	Organisms or recognizable fragments (zooclasts)	Terrestrial	Zoomorphs	Resistant biological remains observed in various stages of fragmentation	Fresh plant litters, acrotelm peat
MYC	Mycelium fragments	Terrestrial	Fungi	Well-preserved fragments observed in various stages of fragmentation	Fresh plant litter, acrotelm peat

Principal information related to their origin, nature, degree of preservation, principal source areas, and, eventually, conditions of formation.

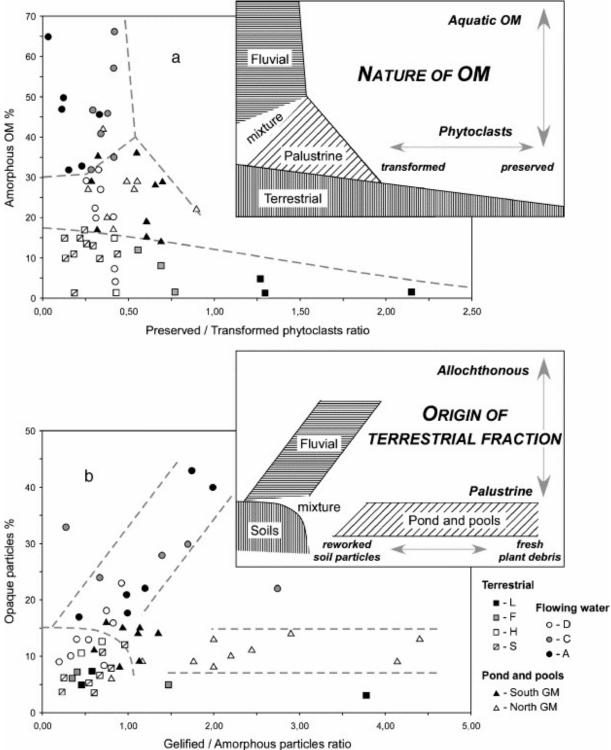


Fig. 6. Characterization of Vernier Marsh deposits with four optical indices (see text) (a) Nature of OM by using "AOM contents" (aquatic or microbial production) and "preserved / transformed phytoclasts ratio" (preservation degree of terrestrial plant debris). (b) Origin of terrestrial fraction by using "OP contents" (allochthonous fraction from fluvial origin) and "GP / AP ratio" (pedogenic or subaquatic degradation of terrestrial plant debris). Lines representing arbitrary boundaries have been plotted for guidance based on the modern environments where the samples were collected.

Some available data from the literature support this conceptual model (<u>Table 3</u>). The soil profiles from various locations show the same trends as those observed in this paper. For terrestrial soil samples, the most significant index is the "preserved phytoclasts / transformed particles ratio" (<u>Table 3</u>). This ratio is highest in fresh litter (> 2.5), then decreases in OF horizons (to about 1.5), and has the lowest values in OH and A horizons (< 0.5). We also note a slight increase of OP contents with depth, there being less than 5% in the surficial layers, and up to 20% in humic layers (<u>Table 3</u>). As shown in previous work (<u>Di Giovanni et al., 1999b</u>), the compositional signature of organo-mineral layers (A horizons) is related to the characteristics of parent-rocks. For example, high AOM contents (> 80%) are observed for the Draix catchment area where the parent-rock is rich in AOM (Di Giovanni, comm. pers.). In the same way, OP contents are high (> 20%) for the Chaillexon catchment area where the parent-rock is rich in OP (<u>Di Giovanni et al., 2000</u>), but lower (> 5%) for Annecy catchment area where the parent-rock is poor in OP (Noël et al., 2001).

Moreover, the four new indices presented in this paper can also be used to analyse the results obtained from Holocene lacustrine (i.e. aquatic environment) or palustrine (i.e. terrestrial environment) deposits (<u>Table 3</u>). The optical signature of micritic limestones from Annecy lake corresponds precisely to an aquatic sedimentation, marked by a significant planktonic contribution (AOM contents about 40%), and a terrestrial contribution marked by materials of detrital origin ("preserved / transformed" and "GP / AP" ratios about 0.4, "OP contents" about 5% to 10%). In addition, the periodic deposition of detrital sediments is recorded by a dilution of the aquatic contributions ("AOM contents" about 30%) and an increase of detrital markers ("OP contents" about 15%; <u>Table 3</u>). When these depositional events are more frequent, we note the appearance of a diagenetic fraction ("GP / AP ratio" about 1.5) derived from terrestrial ("preserved / transformed ratio" about 0.7). In the case of organic facies (i.e. organic mud and peaty deposits, Table 3), the AOM contents are dependent not only on the aquatic contribution (15% in palustrine deposits; 30% in lacustrine deposits from Tritrivakely marsh), but also on a possible contribution of microbial materials (about 50% in organic mud from Annecy lake). In addition, the other indices reflect the preservation state and origin of the terrestrial fraction, and the significance of the detrital inputs.

Table 3. : Mean optical indices calculated from data of the literature  $% \left( 1\right) =\left( 1\right) \left( 1\right) \left($ 

Location	Sample description	n	Optica	ıl indices			Referenc es
			AOM (%)	Preserved / transforme d	Gelified/amorpho us	OP (%)	
Chaillexon catchment (Jura, France)	Recent soil layers						
	Fresh litters (OL horizons)	7	Trace s	3.1	nd	Trace s	
	Fragmentati on layers (OF horizons)	5	Trace s	1.5	nd	6	Di Giovanni et al., 1999a, Di Giovanni et al., 1999b and Di Giovanni et al., 1999c
	Humic layers (OH horizons)	5	Trace s	0.5	nd	20	Di Giovanni et al., 2000
	Organo- mineral layers (A horizons)	4	Trace s	0.3	nd	23	
Draix catchment (Haute- Provence, France)	Recent soil layers						
	Fresh litters (OL horizons)	4	0	4.7	0.3	4	Di Giovanni (not published )
	Humic layers (OH horizons)	5	4	0.3	0.4	15	
	Organo-	4	83	0.1	2.4	6	

Location	Sample description	n	Optica	Il indices			Referenc es
			AOM (%)	Preserved / transforme d	Gelified/amorpho us	OP (%)	
	mineral layers (A horizons)						
Annecy catchment (French Alps)	Recent soil layers						
	Organic layers (OL, OF and OH horizons)	1 3	trace s	2.6	0.2	2	
	Organo- mineral layers (A horizons)	1 3	trace s	0.8	0.1	7	
	Late Holocene lacustrine deposits						
	Micritic limestone	1 3	43	0.4	0.4	6	<u>Noël et</u> al., 2001
	Micritic limestone with some detrital events	7 5	30	0.3	0.2	14	
	Micritic limestone with many detrital events	6	31	0.7	1.5	18	
	Dark organic mud ( <i>gyttja</i> )	4 9	52	1.3	1	9	
Tritrivakely marsh (Madagasc ar)	Late Holocene peaty deposits						
	Palustrine peaty deposits	1 0	15	0.9	0.3	5	Bourdon et al., 2000

Location	Sample description	n	Optica	al indices			Referenc es
			AOM (%)	Preserved / transforme d	Gelified/amorpho us	OP (%)	
	Lacustrine peaty deposits	1 0	30	0.7	0.1	10	

*n*: number of samples.

#### 5.3. Application of optical indices to Holocene deposits

The four new indices presented in this paper were used to characterize the Holocene fluvio-palustrine deposits cored in the Lower Seine Valley (<u>Table 4</u>). Sixty-three samples were analysed and were found to be distributed within fields defined in <u>Fig. 6</u> according to the nature of OM (<u>Fig. 7</u>a) and the origin of the terrestrial fraction (<u>Fig. 7</u>b). Although environments do not exactly correspond to those of the Vernier Marsh, the different optical signatures allow one to discuss the sedimentary OM origin.

Table 4. : Lithology and optical indices of Holocene fluvio-palustrine deposits cored in the Lower Seine Valley (Fig. 1b)

Samples			Optical o	compositional indices		
Lithology	Depth (cm)	TOC (%)	AOM (%)	Preserved/ transformed	Gelified/ amorphous	OP (%)
Clayey loam	1	-	69	0.58	3.33	6
	11	2.3	89	0.03	4.00	5
	21	1.8	90	0.20	3.00	3
	31	2.9	80	0.12	0.50	2
Organic mud	47	17.6	4	0.08	0.83	2
	51	10.9	23	0.12	0.86	2
	59	9.0	20	0.16	1.32	9
Sandy loam	67	0.5	15	0.40	2.22	24

Samples			Optical	compositional indic	ces	
Lithology	Depth (cm)	TOC (%)	AOM (%)	Preserved/ transformed	Gelified/ amorphous	OP (%)
	95	0.7	1	0.19	2.60	48
	105	0.5	1	0.28	1.07	16
Clayey peat	125	17.3	1	0.45	0.34	3
	135	16.8	0	0.39	0.60	2
	145	14.4	0	0.59	0.61	3
	159	15.7	0	0.46	0.33	4
	167	16.1	0	0.66	0.64	4
	177	16.4	0	0.55	0.53	2
	197	18.2	1	0.34	0.50	1
Peat	207	36.9	0	0.12	1.21	2
	227	33.3	0	0.57	0.41	2
	247	39.5	1	0.94	0.38	3
	267	40.1	0	0.52	0.85	1
	277	37.7	0	0.62	0.55	2
	287	39.0	0	1.18	0.69	1
	307	33.1	0	0.76	0.86	1
	317	31.8	1	0.40	0.56	1
Organic mud	327	10.3	1	0.49	0.75	10
	337	10.8	0	1.16	1.29	4
Peat	347	27.8	0	0.53	0.63	5
	367	34.8	0	0.40	0.88	4
	377	39.1	0	0.67	0.42	3
	397	27.4	0	0.42	0.78	2
	407	41.4	0	0.47	0.63	1

Samples			Optical compositional indices			
Lithology	Depth (cm)	TOC (%)	AOM (%)	Preserved/ transformed	Gelified/ amorphous	OP (%)
	417	34.5	1	0.38	0.43	2
Silty sands	425	5.6	1	0.63	0.35	2
	435	1.3	1	0.50	0.26	13
	443	_	16	0.68	0.57	6
	455	2.6	18	0.66	0.67	7
	477	-	18	0.48	1.06	17
	485	3.2	6	0.80	0.37	13

Basal grey silty sands present a signature comparable to that of modern soils (i.e. litter and histosols; Fig. 7) relative to the "preserved / transformed ratio" (> 0.5 and < 0.8) and "GP / AP ratio" (> 0.3 and < 1.1). These older fluvial deposits are interpreted to be related to braided channels where sediments included materials derived from nearly soils that were developed in a forested context based on sedimentological and paleobiological observations (Sebag, 2002). In this case, the amorphous particles represent a paraautochthonous fraction (i.e. reworked from surrounding forested litters). On the other hand, some layers in the basal silty sand seem relatively enriched in aquatic OM ("AOM contents" > 15%) and in strongly oxidized allochthonous particles ("OP contents" > 10%). The main sedimentary body is composed of several meters of peat and clayey peat related to an alluvial backswamp system that was sometimes open to sediment contributions from the Seine River (Sebag, 2002). These deposits present an optical signature that was comparable to that of modern histosols (Fig. 7). The main variations depend on the state and condition of degradation (0.3 < "preserved / transformed ratio" < 1.2; 0.4 < "GP / AP ratio" < 1.5) of the terrestrial fraction. They could be related to local hydrological fluctuations, which controlled the diagenesis of the autochthonous terrestrial fraction. When the groundwater level is low, biodegradation is favoured (low "preserved / transformed ratio") as is the formation of amorphous particles (low values of "GP/AP ratio") involving aerobic processes. When the groundwater level is high, biodegradation is slowed (high values of "preserved / transformed ratio") whereas more anaerobic processes favoured gelification of plant tissues (high values of "GP / AP ratio").

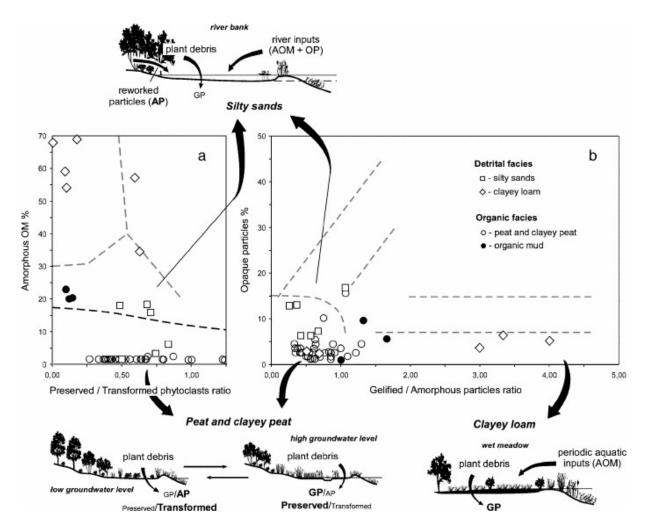


Fig. 7. Characterization of Holocene deposits cored in the Lower Seine Valley with four optical indices (see text). (a) Nature of OM by using "AOM contents" (aquatic or microbial production) and "preserved / transformed phytoclasts ratio" (degree of preservation of terrestrial plant debris). (b) Origin of terrestrial fraction by using "OP contents" (allochthonous fraction from fluvial origin) and "GP / AP ratio" (pedogenic or subaquatic degradation of terrestrial plant debris).

Surficial deposits from the Lower Seine Valley correspond to recent alluvial clayey loams on which wet meadows develop (Sebag, 2002). These layers have high "AOM contents" (> 30%), with some OM of aquatic origin (alluvial deposits). However, the relatively advanced state of degradation and the lack of oxidized particles (i.e. opaque particles) give evidence of the origin of the terrestrial fraction. These characteristics are not linked to an allochthonous fraction transported by water, but are associated with post-sedimentary contributions related to a plant cover developed after deposition.

In this one example, the first two indices ("AOM contents" and "preserved / transformed ratio";  $\underline{\text{Fig. 7a}}$ ) allow one to distinguish three distinct organic assemblages (i.e. terrestrial, mixed or aquatic OM) which are in agreement with the sedimentary record. The "OP contents" show a palustrine signature (OP < 10%) or a mixed signature (OP > 10%). The palustrine samples

are distributed in two fields: (1) a homogeneous group (strictly terrestrial supplies: GP / AP < 1.5) and (2) another group corresponding to various GP / AP values (wet meadows: GP / AP > 1.5). Within each group, the variations of both ratios could be interpreted in terms of depositional environment (i.e. fluctuations of local hydrological conditions).

#### 6. Conclusion

The various optical markers are classically used to study depositional systems that are marked by distinct organic sources. Indeed in the lakes or peaty environments, both autochthonous and allochthonous materials are easily characterized by the results of the palynofacies' analysis. On the other hand, in riparian wetlands, both autochthonous and allochthonous OM sources may be derived from marsh vegetation, fringe forests, algal vegetation, riverine transport of eroded soils and aquatic organisms. Using optical compositional indices allows one to characterize sedimentary organic contents and to compare obviously different samples. In the present study, the results are interpreted in terms of OM origin (i.e. aquatic or terrestrial), source (i.e. autochthonous, para-autochthonous or allochthonous) and diagenesis (i.e. aerobic or anaerobic). This approach could be used to study both sub-recent (i.e. Holocene) and modern fluvio-palustrine deposits. Applied to existing wetlands, such as the Vernier Marsh, this approach leads us to an interpretation of the deposition and redeposition of OM on a landscape scale. Such information is essential to correctly interpret bulk geochemical data that tend to obscure details by averaging results derived from mixed samples. In addition, this kind of study allows one to define a modern frame of reference that can be applied in paleoenvironmental reconstructions, as shown by the compositional indices used in the study of Holocene alluvial deposits.

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