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Soil organic matter (SOM) characterization by Rock-Eval pyrolysis: scope and limitations

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Abstract

Application of Rock-Eval pyrolysis to soil organic matter (SOM) quantitation and characterization has been explored by the study of about 100 soil samples taken from a variety of soil profiles from different ecosystems at different latitudes. A straightforward illustration of these possibilities can be obtained from a Hydrogen Index (HI in mg hydrocarbons g^{-1} TOC) vs. Total Organic Carbon (TOC) diagram that effectively allows one to follow simultaneously the main qualitative (SOM hydrogen richness given by HI values) and quantitative (TOC) changes that affect SOM with increasing depth and humification, in the soil profiles. In addition, abnormally high Oxygen Index (OI in mg CO, CO_2 or O_2 g^{-1} TOC) values are fully diagnostic of extensive SOM alteration, as frequently observed in podzol B horizons. More detailed information on the heterogeneity of SOM and on its degree of evolution, can be gained from the shape of the pyrolysis S2 peak recorded in the course of programmed pyrolysis in an inert atmosphere (N_2) and/or from its maximum temperature "T_{peak}". All these parameters and others, all determined rapidly and automatically, are particularly useful to screen major SOM variations within large sets of samples.

1. Introduction

Interest in the quantitative and qualitative analysis of soil organic matter (SOM) has been motivated by its effective role in evaluating the chemical, biological and physical properties of soils (e.g. van Cleve & Powers, 1995, Karlen et al., 1997, Robert, 1996 and Balesdent, 1996). Another interest has been provided by uncertainties on the effective role of source or sink that soils can effectively play in the global carbon cycle, with for example consequences on the greenhouse effect and climate change (Eswaran et al., 1993, Batjes, 1996, Adams & Faure, 1996 and Carter et al., 1997). For these two reasons, and because of considerable spatial variations in the amount and composition of SOM, there is a need for techniques allowing for its fast and easy quantitation and characterisation. Rock-Eval pyrolysis allows

one to determine the total organic carbon content (TOC wt.%) of rocks and sediments (Espitalite et al., 1977, Espitalite et al., 1985a, Espitalite et al., 1985b and Peters, 1986). The same applies to soil samples (this paper) without the decarbonation required for classical combustion techniques. It also provides information on the composition of the OM, especially through the Hydrogen and Oxygen Index values (HI and OI) much used with other natural organic materials, e.g. kerogens, and known to correlate with H/C and O/C ratios (Espitalié et al., 1985b). Rock-Eval pyrolysis thus provides valuable information on the elemental composition of organic materials that is otherwise difficult to obtain because of the difficulty of isolating the OM without alteration (Stevenson, 1982 and Espitalite et al., 1977). The original goal of Rock-Eval pyrolysis was to rapidly obtain quantitative and qualitative information on the amounts of hydrocarbons and the type of kerogen present in sedimentary rocks, on the degree of thermal maturity of the kerogen and, if possible, on its approximate composition equivalent to that determined by elemental analysis. However, because of the simplicity of this technique it has been used for the analysis of soils and immature sediments (e.g. Disnar & Trichet, 1984, Sifeddine et al., 1995, Ariztegui et al., 1996, Buillit et al., 1997, Di-Giovanni et al., 1998, Di-Giovanni et al., 1999 and Disnar et al., 2000). Here we present results of an analytical survey covering a variety of soils resulting from different soil formation processes, in different continents and with different climates.

2. Materials and methods

2.1. Apparatus

Analyses were carried out with a "Turbo" model RE6 pyrolyzer (Vinci Technologies). The basic operating principles of this apparatus are presented in Fig. 1 and described in Lafargue et al. (1998). Contrary to previous Rock-Eval devices (RE2, RE3) which only measured CO_2, the measurement of CO by RE6 allows one to determine three 'OI's', one for CO_2, one for CO and an additional one for CO_2+CO. This latter parameter called OIRE6, is expressed in mg O_2 g^{-1} TOC.
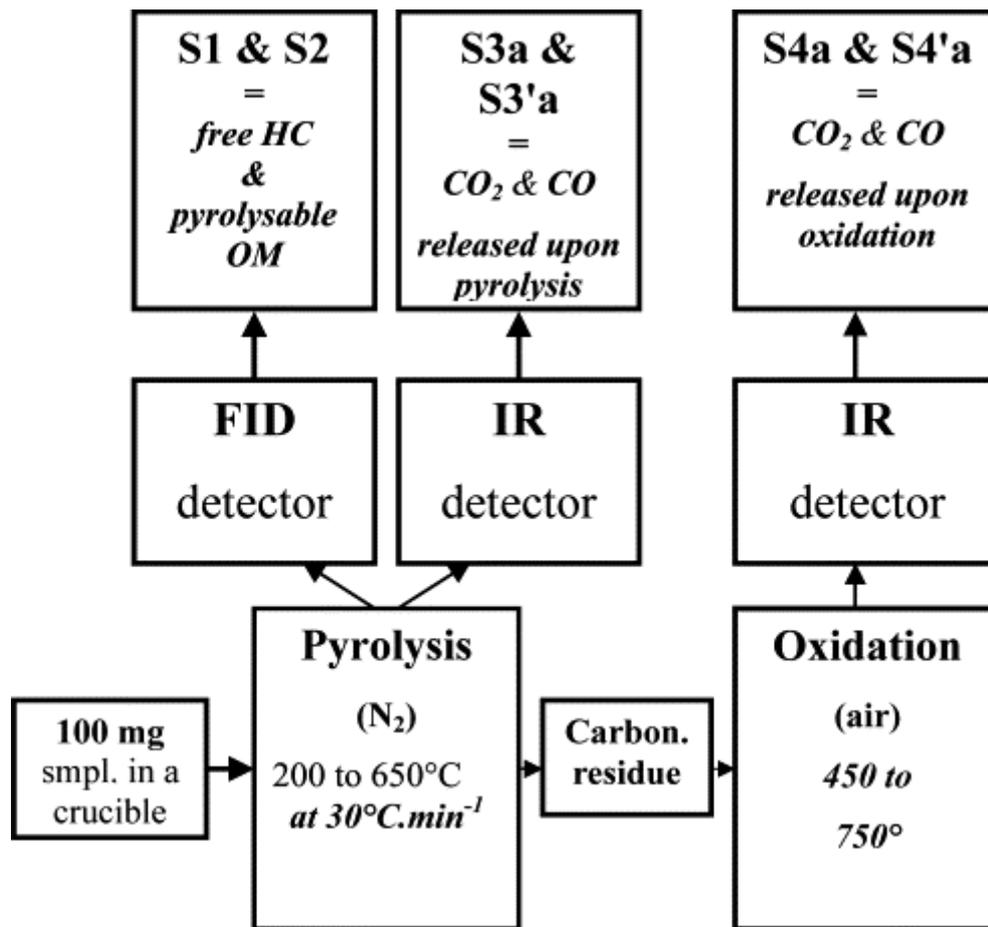
Fig. 1. Operating principles of the Rock-Eval 6 pyrolyzer (RE6)

2.2. Sampling

About 100 samples were collected from 24 different soil profiles of various types. These soils are tabulated (Table 1) according to their occurrence within the main world climate zones. They are named in accordance with the World Reference Base for Soil Resources (FAO, 1994). All soils are acid except chernozems (Ch 75, Ch 79) and phaeozem (Ph 81) which are neutral or basic with calcium-carbonate concretions in the deepest horizons (cf. Ahk in Ch 79). Humus and A horizon samples were collected at less than 35 cm depth from the surface, whereas Bh of podzols and Bt of luvic chenozems were sampled at greater depths.

Table 1. Main characteristics and analytical data on the soil samples studied

Location	Land use	Soil no.	Soil ref. and taxonomy	Horizon	Sample	C Leco (wt.%)	C/N (wt.%)	TOC RE6 (wt.%)	T_{peak} (°C)	T_{max} (°C)	HI (mg HC g^{-1} TOC)	OICO$_2$ (mg CO$_2$ g^{-1} TOC)	OICO (mg CO g^{-1} TOC)	OIRE6 (mg O$_2$ g^{-1} TOC)	HI/OI	R400
Temperate zone under boreal influence Canada Victoriaville	Pine and birch forest	1	Po 39	OL	391	44.4	38.2	39.21	359	319	381	224	70	203	1.88	0.70
			Humic podzol	OF	392	40.9	19.2	36.63	371	331	368	207	61	185	1.99	0.63
				OH	393	32.7	14.5	31.44	370	330	342	206	64	186	1.83	0.47
				A1	394	26.7	18.9	25.03	426	386	338	178	57	162	2.09	0.48
				B21h	124	4.5	26.6	5.59	467	427	84	430	109	375	0.22	0.33
				B22h	125	1.9	21.1	1.98	457	417	91	466	120	408	0.22	0.25
				Bfe	126											
Canada Victoriaville	Pine forest	2	Po 13	B21h	137	2.2	31.8	2.37	469	429	47	308	106	284	0.17	0.27
			Duric podzol	B22h	138	1.8	28.4	1.92	470	430	39	312	107	288	0.14	0.25
Temperate zone under oceanic influence France	Beech forest	3	Cm 44	OL1	442	44.7	23.9	40.20	362	322	336	190	63	174	1.94	0.68
Brittany			Distric cambisol	OL2	443	40.3	15.6	35.74	363	323	373	272	60	232	1.61	0.65
Fougères				OF	444	44.1	21.3	40.57	375	335	336	184	50	163	2.06	0.55
Lowland areas				OH1	445	43.9	21.4	41.19	421	381	299	193	47	168	1.78	0.54
				OH2	446	29.6	19.5	28.01	430	390	311	186	57	167	1.86	0.49
				A1	447	6.4	20.7	6.22	466	426	387	173	41	150	2.59	0.47
France	Oak and holly forest	4	Al 48	OL1	482	47.7[a]	n.d.	40.76	376	336	630	219	60	193	3.26	0.62
Loire valley			Albeluvisol	OL2	483	45.2	37.5	40.39	378	338	420	198	65	181	2.32	0.66
Chambord				OF	484	41.9	24.5	38.46	422	382	345	184	48	161	2.14	0.58
				OH	485	20.9	24.3	19.61	423	383	314	174	51	156	2.01	0.55
				A1	486	3.9	21.1	3.85	431	391	350	168	55	153	2.28	0.55
France	Oak and spruce forest	5	Al 47	OL-OF	471	39.1	21.8	35.34	421	381	333	179	53	161	2.07	0.55
Perche			Albeluvisol	OH	472	29.4	23.0	27.03	425	385	340	182	58	165	2.06	0.52
Freteval				A1	473	10.5	21.0	9.93	463	423	452	157	58	147	3.07	0.47
France	Oak and hornbeam forest	6	Lu 91	OF	913	38.1	20.1	34.30	379	339	379	202	63	183	2.07	0.60
Gâtinais			Typic luvisol	OH	914	25.7	16.9	24.11	377	337	373	206	58	183	2.04	0.55
Montargis				A11	915	3.4	15.3	3.29	466	426	315	201	68	185	1.70	0.41
				A12	916	2.0	15.8	1.98	457	417	330	194	64	177	1.86	0.55
France	Cultivated	7	Lu 71	Ap	711	2.2	13.6	2.13	465	425	256	248	62	216	1.18	0.37
Gâtinais			Albic luvisol	A12	712	0.9	8.3	0.92	455	415	217	263	75	234	0.93	0.31
Montargis				E	713	0.5	7.3	0.50	431	391	117	382	81	324	0.36	0.35
France	Pine forest	8	Po 91	OH	911	39.7	26.6	36.14	424	384	365	169	50	152	2.40	0.57

Location	Land use	Soil no.	Soil ref. and taxonomy	Horizon	Sample	C Leco (wt.%)	C/N (wt.%)	TOC RE6 (wt.%)	T_{peak} (°C)	T_{max} (°C)	HI (mg HC g⁻¹ TOC)	OICO₂ (mg CO₂ g⁻¹ TOC)	OICO (mg CO g⁻¹ TOC)	OIRE6 (mg O₂ g⁻¹ TOC)	HI/OI	R400
Sologne			Umbric podzol with anthric Ah horizons	A1	912	6.9	23.3	6.68	429	389	284	191	60	173	1.64	0.55
Salbris				Ah1	351	1.3	13.7	1.40	472	432	221	150	56	141	1.57	0.95
				Ah2	352	1.2	25.3	1.29	471	431	122	165	64	157	0.78	0.34
				B21h	353	1.8	33.7	1.85	463	423	57	241	80	221	0.26	0.32
				B22h	354	0.5	18.9	0.61	451	411	30	203	64	184	0.16	0.38

Temperate zone under oceanic influence

Highland areas

Location	Land use	Soil no.	Soil ref. and taxonomy	Horizon	Sample	C Leco (wt.%)	C/N (wt.%)	TOC RE6 (wt.%)	T_{peak} (°C)	T_{max} (°C)	HI (mg HC g⁻¹ TOC)	OICO₂ (mg CO₂ g⁻¹ TOC)	OICO (mg CO g⁻¹ TOC)	OIRE6 (mg O₂ g⁻¹ TOC)	HI/OI	R400
France	Spruce forest	9	Cm 20	OL	201	44.9	35.7	39.82	384	344	428	172	75	168	2.55	0.56
Massif Central			Folic cambisol	OF	202	30.3	17.8	28.19	376	336	372	193	61	175	2.13	0.55
Mont-Lozère				OH	203	11.7	14.5	11.19	471	431	261	206	67	188	1.39	0.52
				A11	204	5.1	13.6	4.98	461	421	229	192	62	175	1.31	0.44
				A1-Bw	207	4.2	12.6	4.06	468	428	164	196	53	173	0.95	0.35
France	Spruce forest	10	Cm 53	OF	531	32.4	21.8	30.24	424	384	338	182	61	167	2.03	0.53
Massif Central			Spodic cambisol	OH	532	22.3	21.6	20.63	422	382	332	200	64	182	1.82	0.54
Mont-Lozère				A11	533	3.8	17.2	3.92	469	429	215	253	75	227	0.95	0.42
				A12	534	4.5	14.2	4.68	443	403	217	244	76	221	0.99	0.41
				A13	535	3.9	16.8	3.88	470	430	196	241	77	220	0.89	0.42
				A1-Bw	537	2.6	15.4	2.67	471	431	176	249	87	231	0.76	0.32
France	Beech forest	11	Le 52	OL-OF	521	39.0	31.8	34.95	384	344	363	180	71	172	2.12	0.69
Massif Central			Folic leptosol	OH	523	28.4	19.7	28.48	422	382	317	200	67	184	1.72	0.55
Mont-Lozère				A11	524	5.7	20.6	5.89	470	430	188	236	77	216	0.87	0.39
				A13	526	4.6	21.3	4.64	472	432	177	245	81	224	0.79	0.30
				A14	527	3.6	20.6	3.59	470	430	198	258	84	236	0.84	0.29
France	Beech forest	12	An 93	A11	931	11.5	11.9	10.92	472	432	159	327	84	286	0.55	0.36
Massif Central			Mollic andosol	A12	932	9.1	12.2	8.85	471	431	121	365	88	316	0.38	0.25
Puy Mercoeur				A13	933	8.8	12.5	8.80	472	432	115	365	85	314	0.37	0.25
				A1-Bw	934	5.7	13.5	5.62	472	432	95	442	92	374	0.25	0.21
France	Beech forest	13	An 16	A1	161	7.0	14.7	6.82	470	430	156	295	87	264	0.59	0.33
Massif Central			Cambic andosol	A1-Bw	162	n.d.	n.d.	3.12	465	425	90	407	102	354	0.25	0.26
Le Bouchet																

Temperate zone under continental influence

Location	Land use	Soil no.	Soil ref. and taxonomy	Horizon	Sample	C Leco (wt.%)	C/N (wt.%)	TOC RE6 (wt.%)	T_{peak} (°C)	T_{max} (°C)	HI (mg HC g⁻¹ TOC)	OICO₂ (mg CO₂ g⁻¹ TOC)	OICO (mg CO g⁻¹ TOC)	OIRE6 (mg O₂ g⁻¹ TOC)	HI/OI	R400
Roumania	Cultivated	14	Ch 75	Ah1	751	2.3	12.2	2.30	427	387	45	195	53	172	0.26	0.38

Location	Land use	Soil no.	Soil ref. and taxonomy	Horizon	Sample	C Leco (wt.%)	C/N (wt.%)	TOC RE6 (wt.%)	T_{peak} (°C)	T_{max} (°C)	HI (mg HC g⁻¹ TOC)	OICO$_2$ (mg CO$_2$ g⁻¹ TOC)	OICO (mg CO g⁻¹ TOC)	OIRE6 (mg O$_2$ g⁻¹ TOC)	HI/OI	R400
Baltati			Luvic chernozem	Ah2	752	2.1	13.3	1.99	436	396	39	207	50	179	0.22	0.36
				Bt	753	1.4	12.2	1.37	403	363	35	216	59	191	0.18	0.33
Bulgaria Gritvitsa	Mixed oak forest	15	Ph 81 Luvic phaeozem	A1	811	3.5	10.2	3.45	453	413	164	235	77	214	0.76	0.40
				Bt1	812	0.8	6.7	0.82	401	361	72	330	113	305	0.23	0.38
				Bt	813	0.6	5.6	0.54	402	362	59	438	130	393	0.15	0.34
Bulgarie Trastenik	Cultivated	16	Ch 79 Calcic chernozem	Ah1	791	1.6	13.0	1.52	446	406	87	130	70	135	0.65	0.31
				Ah2k	792	1.2	15.1	1.26	467	427	116	319	69	271	0.43	0.26
				Ah3k	793	1.0	19.5	0.86	450	410	87	403	78	338	0.26	0.31
Tropical zone Highland areas																
Colombia Bogota Sapo	Grassland	17	Fe 86 Eutric ferralsol	Ah1	861	2.4	9.2	2.27	465	425	179	254	69	224	0.80	0.40
								0.00								
Colombia Bogota Suesca	Grassland	18	Fe 85 Eutric ferralsol	Ah1	851	3.4	15.3	3.21	513	473	51	346	87	302	0.17	0.16
				Ah2	852	3.5	22.1	3.69	473	433	63	266	71	234	0.27	n.d.
Tropical zone Lowland areas																
Cameroun Bertoua Kandara	Savanna	19	Fe 89 Dysric ferralsol	OL-OF	891	41.7[a]	48.1	35.60	347	307	409	263	104	251	1.63	0.80
				A11	892	2.7	12.3	2.70	454	414	91	220	80	206	0.44	0.39
				A12	893	1.3	9.2	1.21	445	405	105	341	125	319	0.33	0.36
Cameroun Bertoua Kandara	Semi-deciduous forest	20	Fe 90 Dystric ferrasol	OL-OF	901	43.6[a]	20.7	37.57	353	313	410	268	75	238	1.73	0.75
				OH	902	34.5	12.7	31.56	372	332	335	230	65	204	1.64	0.61
				A11	903	5.0	11.3	4.79	456	416	175	230	69	207	0.85	0.39
				A12	904	1.8	8.9	1.73	443	403	105	291	81	258	0.41	0.36
Congo Pointe Noire	Savanna	21	Ar 87 Ferralic arenosol	OL	871	5.8	17.3	5.46	324	284	335	152	74	153	2.19	0.63
				A11	872	0.7	7.2	0.69	453	413	173	219	66	197	0.88	0.54
				A12	873	0.6	8.1	0.60	456	416	144	239	68	212	0.68	0.42
				A13	874	0.4	6.7	0.47	456	416	182	259	70	229	0.80	0.45
Congo Pointe Noire	Eucalyptus plantation	22	Ar 88 Ferralic arenosol	OL	881	51.3[a]	71.5	44.21	371	331	482	156	45	139	3.46	0.65
				A11	882	1.0	9.9	0.93	452	412	186	240	71	215	0.86	0.43
				A12	883	0.5	5.7	0.40	450	410	93	306	63	258	0.36	0.39
				A13	884	0.4	4.4	0.32	447	407	90	321	68	273	0.33	0.41
Congo Pointe Noire	Savanna	23	Po 83 Duric podzol	A11	831	1.3	17.0	1.26	471	431	452	139	46	127	3.55	0.39
				A12	832	0.3	4.9	0.29	327	287	227	192	65	177	1.28	0.57
				B21h	833	1.1	16.6	1.20	459	419	64	152	45	137	0.47	0.36
				B22h	834	2.0	36.6	2.09	445	405	36	166	77	164	0.22	0.35
Congo Brazzaville	Savanna	24	Po 14 Humic podzol	B21h	141	5.2	49.9	6.28	455	415	35	166	98	177	0.20	0.26
				B22h	142	2.5	22.5	2.25	470	4						

n.d.=Not determined.

a C (wt.%) value of litter sample rather strongly underestimated by RE6 pyrolysis.

The cold and humid climate of the boreal Canadian zone is favourable for podzol development on glacial till or crystalline bedrock poor in clay and weathered minerals. Forest soils present humus of moder or mor type including a thick OH horizon rich in faecal pellets, overlying an A1 horizon comprising organic aggregates juxtaposed to quartz grains. Spodic B21h and B22h horizons result from the accumulation of organic-Fe-Al complexes translocated through eluvial horizons from the humus layers. In such spodic horizons, organic matter forms either grain coatings causing a strong skeleton grain cementation (Po 13) or aggregates originating from root decay (*cf.* samples nos. 124 and 125 in Po 39).

In lowland areas of the temperate zone (Table 1), soils developed on loamy materials are frequently cultivated. We sampled only one of them (Lu 71) in the vicinity of a forest profile (Lu 91) from which it derives by clearfelling and cultivation. We also collected topsoil profiles in deciduous forests of beech (*Fagus silvatica*, cf. Cm 44), of oak (*Quercus sessiliflora*) somewhere mixed with indigenous holly (*Ilex aquifolium*, cf. Al 48) or with planted conifers such as spruce (*Picea abies*, cf. Al 47). Humus were moder from which we separated OL, OF and OH horizons, especially in oak and beech forests. The thickness of the OH horizon varied from 0.5 to 2 cm.

Whereas boreal zone podzolization is a climatic process, in temperate and even tropical climate zones, podzols might have developed provided that parent materials were poor in alterable minerals. Thus, umbric podzols (Po 91) have developed on Tertiary sands, under *Pinus* sp, in Sologne (Fr). Such soils have developed thick humus as well as anthric Ah horizons and Bh, during a past heathland phase.

Soil profiles of highland areas of the temperate zone were collected under forests in the Massif Central (France). Cambisols (Cm 20, Cm 53) and leptosol (Le 52) rich in TOC, have been formed under beech or spruce on granite at Mont Lozère (1.300–1.400 m elevation) whereas andosols (An 93, An 16) have developed under beech on basalt in the "Chaine des Puys" (1.200 m elev.). Cambisols and leptosol frequently display a thick moder OH horizon with a C/N value of about 20 which decreases slightly in the underlying A1 horizons. In contrast, andosols have a mollic epipedon corresponding to a mull type humus. In such soils the beech litter is quickly degraded, and there is incorporation of much organic matter in all horizons, even in the deepest ones.

In the temperate zones under continental influence (Table 1), chernozems (Ch 75, Ch 79) cover a large surface of Eurasian steppes in association with phaeozems (Ph 81) which are present in most humid areas where deciduous forests were preserved. These soils are characterized by their dark brown mollic horizons, much grass root production and intense biological activity, especially of earthworms, in frequently cultivated chernozems. Despite their blackish color, these soils have low TOC contents and C/N values.

In tropical zones, there is diversity of soil-forming processes because climates, parent materials and pedogenesis vary from one area to another. We sampled three locations in Colombia, Cameroon and Congo. Eutric ferralsols (Fe 85, Fe 86) sampled in the Colombian oriental cordillera near Bogota support tall grass savannas (Guillet et al., 1988). In Cameroon,

two dystric ferralsol profiles (Fe 89, Fe 90) were sampled in a tall grass savanna and in an adjacent semi-deciduous forest which encroached on the savanna less than 100 years ago (Guillet et al., 2001). Excluding litter fragments (OL-OF, OH), the top-soil A11 and A12 horizons present a sandy clay texture consisting of about 50% of clay minerals. Intense biological activity within the first 25 cm explains the relatively high TOC contents and low C/N values, especially in forests. Arenosol profiles (Ar 87, Ar 88) collected in the Congo are typical ferralitic soils developed on sandy parent materials poor in clay. Contrasting with Cameroonian soils, there is a small accumulation of organic matter in topsoil, probably due to the insufficient adsorbing properties of kaolinite-type clay minerals. On such very poor parent materials giant podzols (Po 14, Po 83) were observed in the Congo (Schwartz, 1988). These soils present thick and indurated B21h and B22h horizons poor in organic nitrogen. Some of them presently in savanna are fossil podzols that developed in a formerly hydromorphous forest environment (Schwartz et al., 1986).

3. Results and discussion

3.1. TOC (%) determination and limitations

One advantage of Rock-Eval pyrolysis is to provide TOC values without preliminary treatment such as decarbonatation as required for the determination of the organic carbon by classical combustion techniques. As shown in Fig. 2, there is a very good correlation (R^2=0.998) between TOC values determined by Rock-Eval 6 and in carbonate-free samples on a Leco analyser. However, the Rock-Eval TOC values are, on average, 9.16% lower on a relative basis, than those determined by the Leco technique. This difference arises because of a lower response of the FID detector to the hydrogen-poor SOM pyrolysates than to those of the 55 000 IFP marl standard. In addition, part of the SOM hydrogen is probably lost as H_2O, not detected by the FID, as a result of dehydration reactions. This general interpretation is substantiated by the fact that the greatest discrepancy between the two techniques is usually observed for litter samples. Such samples are rich in carbon but with notable proportions of cellulose and other polysaccharides which easily lose water on heating. Under more drastic heating these polymers decompose giving oxygenated compounds, e.g. furfurals, that produce a lower FID response than fully hydrogenated moieties. One way to solve the TOC problem is to use a more adequate standard than IFP 55 000. The other way is to keep the same standard, to avoid any confusion, but to correct the experimental data by a constant factor. After the correlation presented in Fig. 2, the experimental TOC values must be divided by 0.916 (or multiplied by 1.092). A supplementary correcting factor (1.068) should be specifically applied to biopolymer-rich samples of forest soil litter (e.g. samples 482, 881, 891, 901 in Table 1). No correction has been made in this paper.
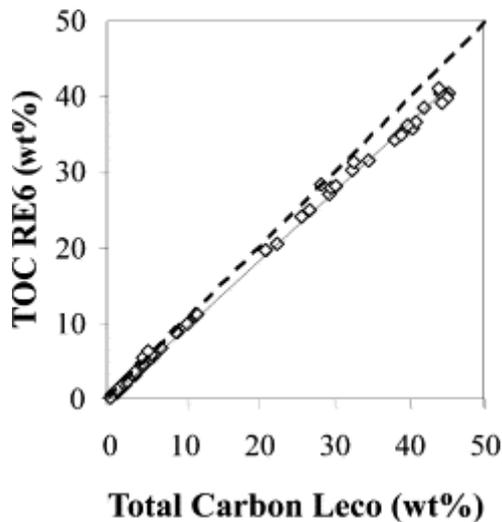
Fig. 2. Correlation between TOC contents (%) determined by RE6 pyrolysis (+ oxidation) with Total carbon contents determined by classical combustion with a Leco CNS-2000 analyzer. The absence of carbonates in the samples allows for the direct comparison of Total carbon Leco determinations with RE6 TOC measurements. The samples of fresh litter nos. 482, 881, 891 and 901 (Table 1) have not been taken into account for this comparison (see text).

The data presented in Fig. 2 already allows one to appreciate the precision of the method. Replicate analyses of soil samples show excellent TOC reproducibility, with an analytical error normally lower than 2% (Disnar et al., 2000).

The use of TOC values for characterising SOM and distinguishing soil profiles will be discussed later, together with HI and OI results.

The standard deviation on the other main parameters are: $T_{peak}\pm5$ °C ; HI:±6% ; OI RE6:±10%.

3.2. Free hydrocarbonaceous compounds (S1 peak)

Except in case of contamination by low molecular weight organics, S1 is usually minor in soils and can thus generally be neglected.

3.3. Hydrogen and oxygen index values (HI and OI)

Previous work on kerogen has demonstrated that the Hydrogen Index and Oxygen Index values correlate with atomic H/C and O/C values, respectively (Espitalié et al., 1977). The determination of such correlations requires one to determine the elemental composition of a large set of samples free of mineral matter. Such samples are very difficult to obtain from soils because the isolation treatment considerably alters recent organic material (Stevenson, 1982).

Before further discussing the data, two points are worth mentioning. First, analysis of TOC-poor rock samples frequently show a decrease of HI values with decreasing TOC. Thus, S2 vs. TOC plots generally show a correlation curve that intercepts the abscissa axis (Langford and Blanc-Valleron, 1990). This phenomenon may result from successive retention and dehydrogenation of increasing proportions of pyrolysis products by the mineral matrix, with

decreasing TOC content (Espitalite et al., 1984 and Espitalite et al., 1985b). Clays and especially illite and attapulgite have the most pronounced effect whereas kaolinite is almost completely inactive (Makadi Kimpanga, 1982 and Espitalite et al., 1984). As examplified in Fig. 3, for soils, the S2 vs. TOC correlation curve that tends towards the origin of the axes indicates that there is no noticeable mineral matrix effect and thus no alteration of HI values for SOM-poor samples. This might firstly result from the absence of active mineral species in the corresponding A and B horizons, and secondly also from the low dehydrogenation capacity of the already hydrogen-poor SOM and of its pyrolysis products.
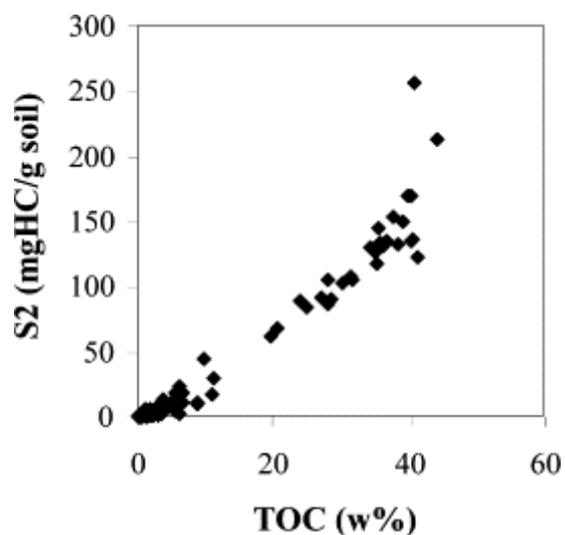
Fig. 3. Pyrolysable SOM contents (S2 in mg HC g^{-1} sample) vs. TOC (%) for the soil samples studied.

The second remark concerns the oxygen index OI, or more precisely the three different oxygen indexes that can be determined by RE6 (see Experimental). The data presented in Table 1 show that IOCO varies much less (i.e. by factor two) than $OICO_2$ and that this latter is much greater than OICO (about 3 times as a mean). Despite the fact that OIRE6 and $OICO_2$ are not strictly equivalent (even if CO is relatively minor with regard to CO_2) and in addition, that they are not expressed in the same units (mg CO_2 g^{-1} TOC vs. mg O_2 g^{-1} TOC) their correlation and their close numerical values allow us to use the one or the other in soil analysis (Fig. 4).
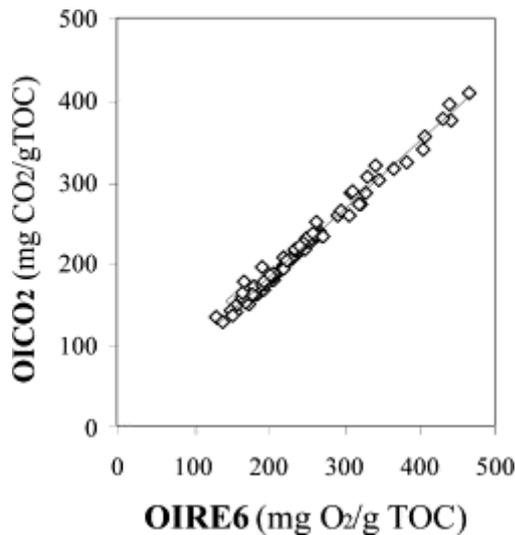
Fig. 4. Comparison between OIRE6 and OICO2 values showing the high degree of correlation between these two parameters.

When plotted in an HI vs. OI diagram, the data corresponding to the various soil horizons mostly show decreasing HI values with increasing depth in the soil profiles and thus increasing humification (Fig. 5). OI values show increasing scattering from the upper layers, down to the B horizon in which SOM only displays residual HI values of 100 or less, and variable but generally high OIRE6 values of 100–400 mg O_2 g^{-1} TOC. The downward general evolution trend exhibited by SOM is comparable to that experienced by weathered coals (e.g. Lo and Cardott, 1995). It consists in a progressive oxidation that begins with dehydrogenation (i.e. HI decreases) and eventually goes on with a gain in oxygen (i.e. OI increases). This latter phenomenon is especially well marked in podzol B horizons where SOM has also been oxidised in the course of humification and/or as a result of humic substance illuviation (Fig. 5). The gross transformations of SOM depicted by HI and OI variations can also be compared to the C/N ratio. As illustrated in Fig. 6, the mineralisation of polysaccharides and other N-poor biopolymers is responsible for the decrease of the C/N ratio in the top soil layers (OL, OF), without any marked HI decrease. With large variations depending on individual sites the SOM from A horizon samples globally presents rather low HI and C/N values as a result of strong alteration. In contrast, in the underlying B horizons in podzols, the SOM presents still lower HI and frequently higher C/N ratio values. The latter are typical for the N-poor highly oxygenated compounds that accumulate in such horizons (e.g. Andreux et al., 1986).
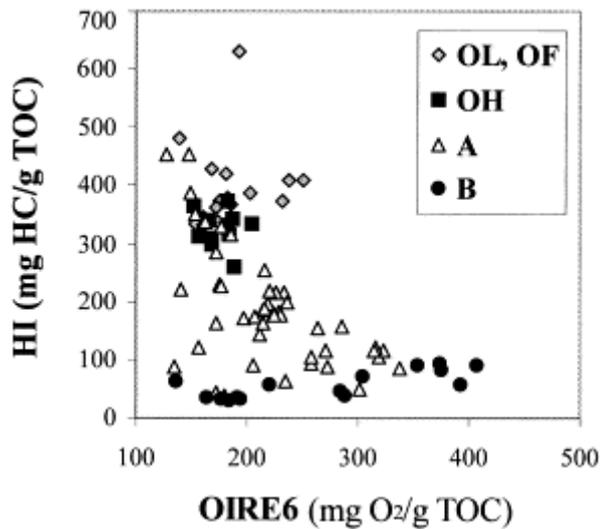
Fig. 5. HI vs. OI diagram (comparable to the classical Van Krevelen H/C vs. O/C diagram).
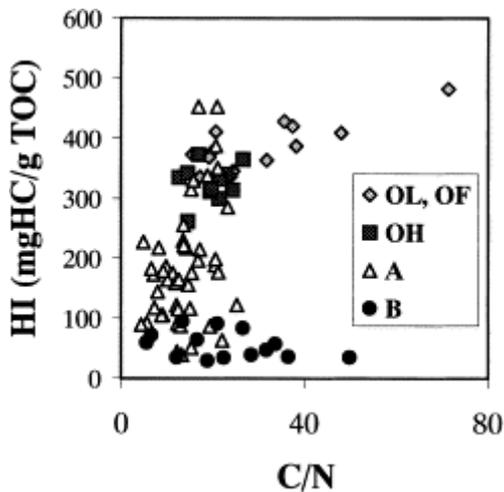
Fig. 6. HI vs. C/N diagram.

A more useful presentation than the HI vs. OI plot might be an HI vs. TOC diagram (Fig. 7). This allows one to appreciate the main variations in SOM quality given by HI values, together with those in TOC contents, mostly governed by the mineralisation of SOM and its dilution by the mineral matrix. All the samples of fresh and fragmented litter (OL and OF) normally show high TOC values (10–40%) and HI values higher than 300 mg HC g^{-1} TOC. Such HI values are expected for minimally transformed terrestrial plant material rich in polysaccharides, lignin and other biopolymers. Because the transformation of the original biological inputs in the litter is small, the scattering of the corresponding data points mostly originates from the variation in composition of the parent plants. This is illustrated in Fig. 7 by a sample of litter of holly and oak which displays a very high HI value (>600 mg HC g^{-1} TOC) demonstrating the richness of the holly waxes. Generally, the OH soil layers display only slightly lower TOC and HI values than those of the litter. These comparable values illustrate the fact that in OH layers the SOM is formed of vegetal debris completely comminuted by the mesofauna, but (bio-)chemically little transformed (Zech & Kogel-Knabner, 1994 and Disnar et al., 2001a).
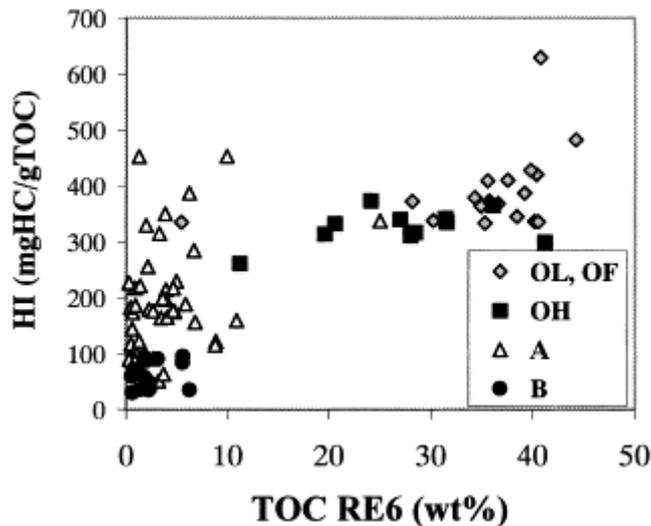
Fig. 7. HI vs. TOC diagram.

More important changes occur in the organo-mineral A horizon but with considerable variations from one soil to another as shown by HI values (Table 1) varying between 450 (e.g. soil Al 47) and 50 mg HC g^{-1} TOC (e.g. chernozem Ch 75 and ferrasol Fe 85). At the same time, TOC values vary between less than 0.5 (e.g. arenosols) and more than 10 (up to about 25 if one consider a sample of podzol—no. 394—identified as an Ah) (Table 1). This scattering results from the multiplicity of soil uses, the nature of the fine mineral fractions and uncertainties in the distinction of layers and horizons (Federer, 1982). As expected, rather high HI values are found in the top layer of the organo-mineral horizons of soil profiles due to a moder type humus where, by definition, there is no clear cut distinction between the humus layer and the underlying A1 layer (Jabiol et al., 1995). Thus, the SOM in the latter should mostly differ from that of the OH layer as a result of greater dilution by the mineral matrix, i.e. from a quantitative (TOC) rather than a qualitative (HI). Then, the corresponding rather high HI values mostly result from the slight transformation of the vegetal inputs due to rather low biological activity. In clay-poor soils such as sandy podzols developed under savannah high HI values are found in the A1 horizon (e.g. 452 in A11; sample 831, profile Po 83; Table 1). In A1 horizons in such sandy soils, SOM occurs as pellets formed by the active fauna. These pellets are juxtaposed but not intermingled in the mineral matrix. In most cases, SOM quantity and quality decrease with increasing depth. HI values lower that 100 are reached in the deepest layers of the A horizon and/or in the underlying spodic or cambic horizon (B). A drawback of this diagrammatic representation is that it only partly accounts for the oxidation undergone by SOM in the course of humification, i.e. the loss of hydrogen expressed by the lowering of the HI, but not the subsequent oxygen uptake responsible for the rise of the OI. The parameter HI/OI formally related to an atomic H/O ratio should better express the continuity of the oxidation phenomenon since it first decreases with decreasing HI, then continues to decrease with increasing OI (here taken as OI RE6). As demonstrated in Table 1, the HI/ OI ratio values of the OL, OF and OH layers which contain relatively little transformed biopolymers are all equal or greater than 1.4. In contrast, samples from podzol B horizons containing highly functionalized water-soluble organics have ratios around 0.2±0.1 (with one value approaching 0.5; Table 1) (Anderson, 1979). HI/OI values of intermediate A horizons are largely scattered between these two extremes. However high values (>1.4) are found in savanna top soil, most probably due to the presence of slightly degraded plant debris (sample 831; Table 1). High HI/OI values recorded in A1 layers of soils having developed a

mor or moder type humus are consistent with the slow SOM transformation typical of such situations (samples 473, 447, 486, 394, 916, 915, 912 and 351; Table 1).

3.4. T_{max} and shape of the pyrolysis S2 peak

T_{max} which corresponds to the oven temperature at the maximum of the S2 peak is a well-known maturity indicator (Espitalite et al., 1985a, Espitalite et al., 1985b and Disnar, 1994). It increases regularly with increasing burial, provided that the OM has previously reached or passed the onset of the main oil generation stage (T_{max}>430–435 °C). Before that stage the OM is simply said to be immature. It is important to stress that T_{max} is about 40 °C lower than the real temperature experienced by the sample at the time it was recorded due to misplacement of the oven temperature probe in previous Rock-Eval instruments, especially in RE2 (Espitalié et al., 1985a). This problem has been corrected in Rock-Eval 6, which records the temperatures experienced by the sample. To avoid any confusion with T_{max} the corresponding true operating temperature is called "T_{peak}". However, because geochemists are used to T_{max}-based temperatures, the Rock-Eval 6 also accordingly "corrects" pyrolysis temperature to provide the older values. However, since T_{max} has no particular meaning for soil scientists we prefer T_{peak} values which have a straightforward significance and allow a more direct comparison with pyrolysis temperatures in other instruments (e.g. Schnitzer et al., 1994 and Jocter-Montrozier & Robin, 1988).

In immature samples the S2 peak is frequently non-gaussian and can be accompanied with shoulders. The T_{max}/T_{peak} value given the Rock-Eval corresponds to the highest peak. Previous work on recent OM has demonstrated that these various peaks or shoulders correspond to the successive cracking of organic components of different thermal stabilities (e.g. glucides before polypeptides) (Disnar, 1982 and Disnar & Trichet, 1984). This interpretation is here fully consistent with the very low T_{peak} values of 320 to 390 °C found in the upper layers of the soils studied, i.e. OL, OF and some of the OH layers (Fig. 8). These low values are typical for the thermal breakdown of biological constituents such as polysaccharides and lignin (Fig. 9) and thus reflect the predominance of original compounds in the topsoil layers. In contrast, the T_{peak} of 420 to 470 °C observed in the A and B horizons (Fig. 8) are typical of immature humic substances. As shown in Fig. 10 this distinction is well evidenced by the results of the mathematical deconvolution of S2 peaks from a few soil profiles. A detailed interpretation of the results of such a treatment is rather difficult because of the variability of biological sources and soil environments. The first peak or shoulder is at a T_{peak} of 300 to 320 °C. It is seldom dominant and is caused by thermally labile biological compounds (Bigois et al., 1986 and Jocter-Montrozier & Robin, 1988). The T_{peak} at 360–370 °C, frequently observed in litter (OL and OF; Fig. 8) samples, is mostly attributed to cellulose and/or lignin, two major components of woody tissues (Fig. 9), or even to other biopolymers such as polypeptides (Disnar and Trichet, 1984). The pyrolysis of these biological compounds is virtually achieved at 400 °C (360 °C T_{max}-equivalent temperature) while humic substances decompose at T_{peak} values of about 420 °C and/or 440 to 470 °C as observed in most OH layers and all A and B horizons (Fig 8 and Fig. 10). In consequence, the proportion of the S2 peak integrated before 400° (T_{peak} equivalent temperature) referred to as parameter R400 in Table 1 (which should mostly depend on the proportions of biomolecules) should decrease with depth in soil profiles. This is shown by the general decrease of R400 values with depth, as in the soil profiles studied (Table 1). A further confirmation of this is given by the correlation between HI/OI and R400 values (Fig. 11). The roughly parallel change of these parameters expresses the simultaneous change of the elemental composition of the SOM structure, through the formation of humic-like substances from biopolymers. Accordingly,

both these parameters display high values in the OL and OF topsoil layers which mostly contains hydrogen-rich biomolecules. They both change markedly in A horizons especially around HI/OI values of 1.4 and R400 values of 0.5, respectively. This latter value might thus be taken to indicate a major stage in the transformation of SOM.
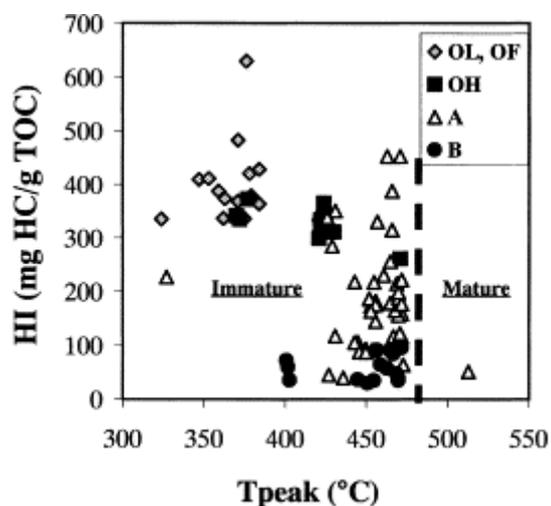

Fig 8. HI vs. T_{peak} diagram. T_{peak} is the accurate temperature experienced by the sample when producing the maximum amount of hydrocarbons (S2 peak) during pyrolysis in a RE6 instrument. The more classical T_{max} values obtained from previous Rock-Eval models are 40 °C lower than T_{peak} temperatures (see text).
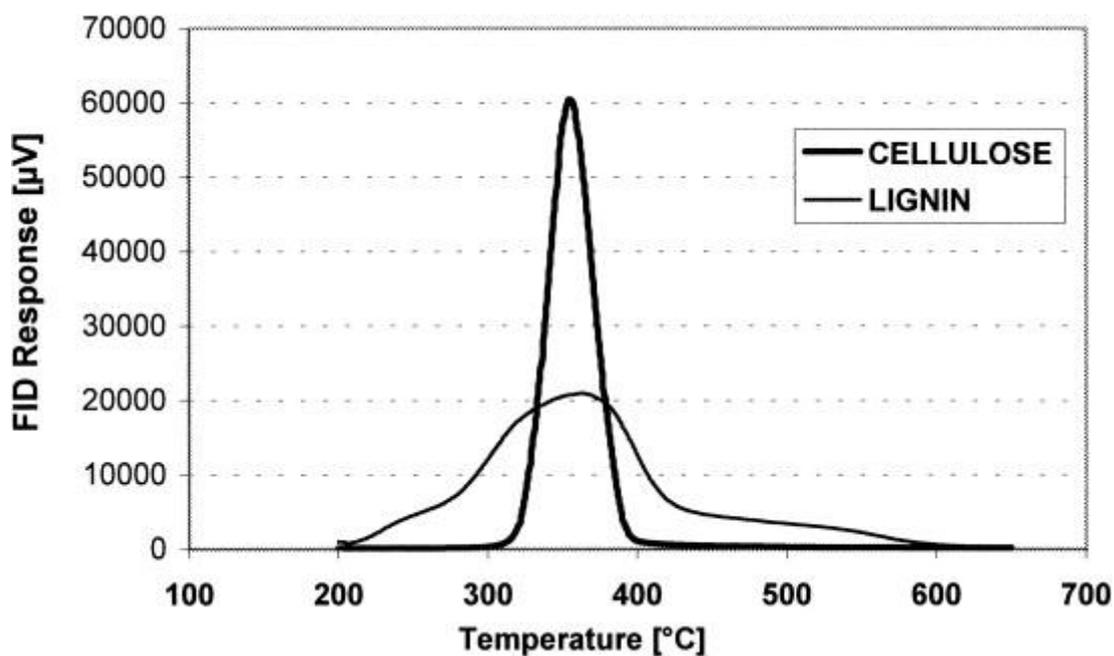
Fig. 9. Pyrograms (S2 signals) of pure cellulose and lignin.

(a)

OL $R^2=0.999$ — PODZOL - Po 39
304, 363, 424, 480

OF $R^2=0.998$
308, 370, 439, 482

OH $R^2=0.999$
309, 368, 434, 481

A1 $R^2=0.992$
308, 370, 434, 478

B21h $R^2=0.997$
309, 375, 455, 513

B22h $R^2=0.996$
302, 379, 454, 503

Temperature (°C)
Intensity

(b) SPODIC CAMBISOL - Cm 53

OF, $R^2=0.995$; peaks at 306, 375, 432, 476

OH, $R^2=0.997$; peaks at 290, 361, 439, 480

A11, $R^2=0.990$; peaks at 309, 369, 437, 478

A12, $R^2=0.987$; peaks at 308, 371, 436, 474

A13, $R^2=0.980$; peaks at 305, 369, 439, 481

A1 - Bw, $R^2=0.991$; peaks at 309, 372, 438, 481
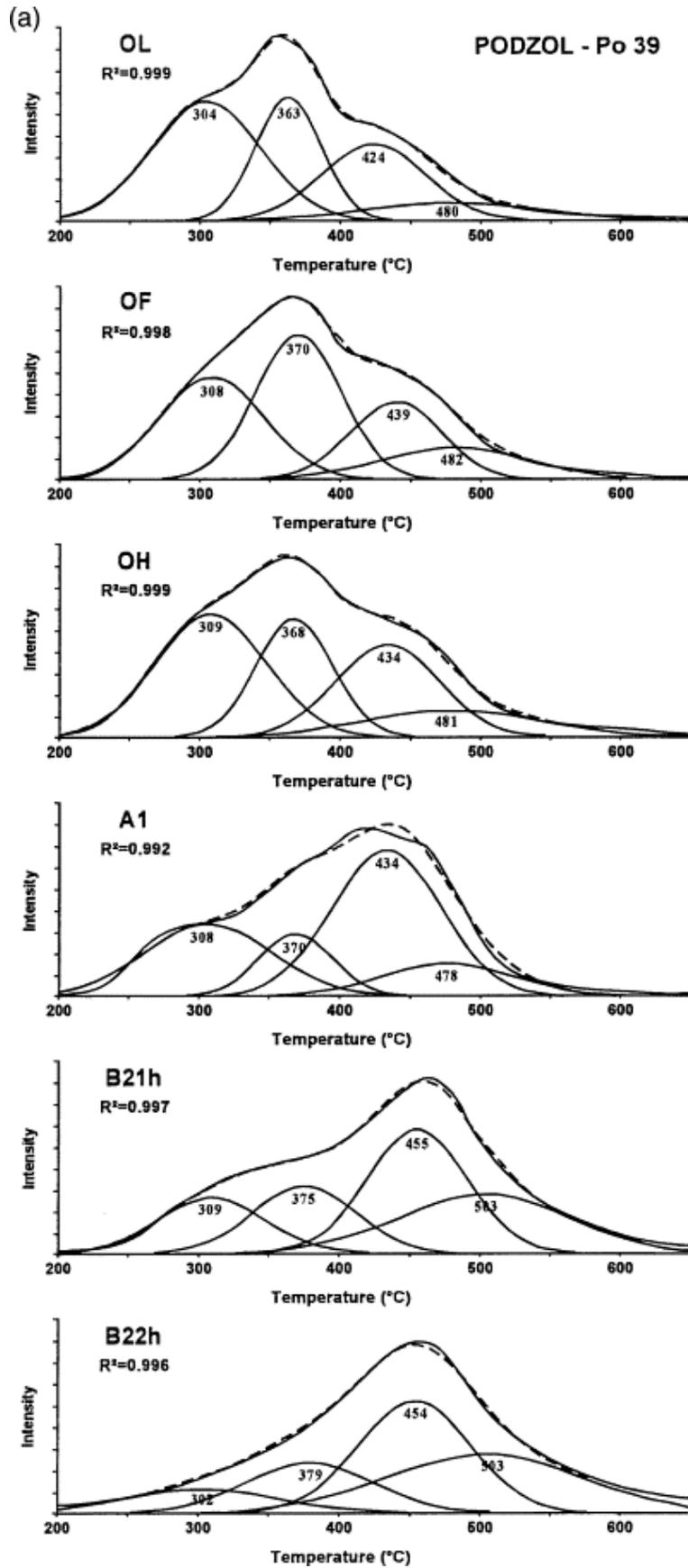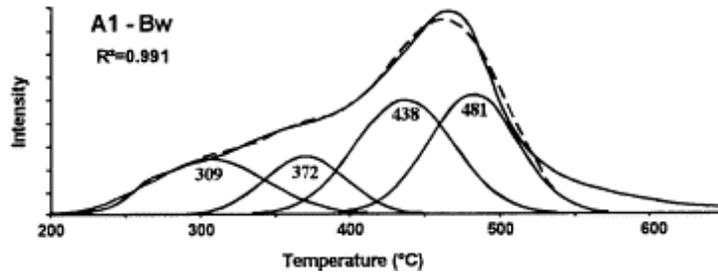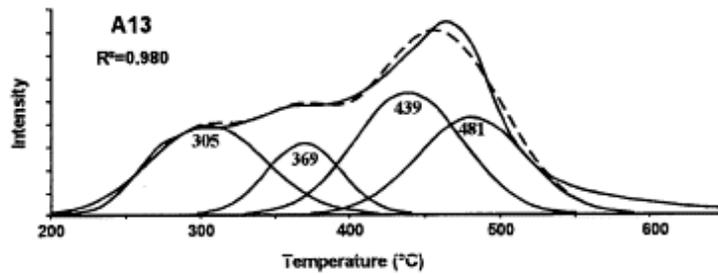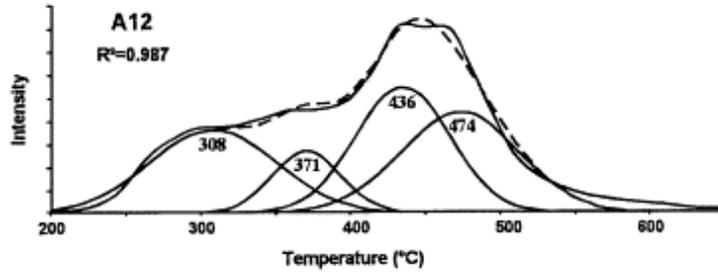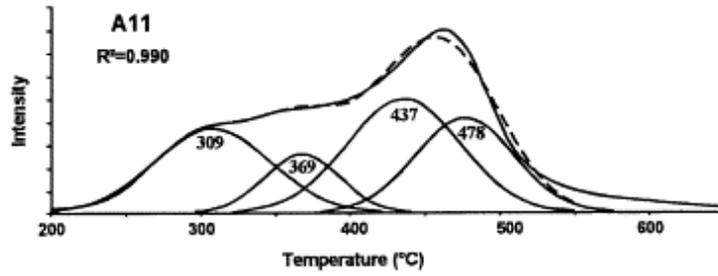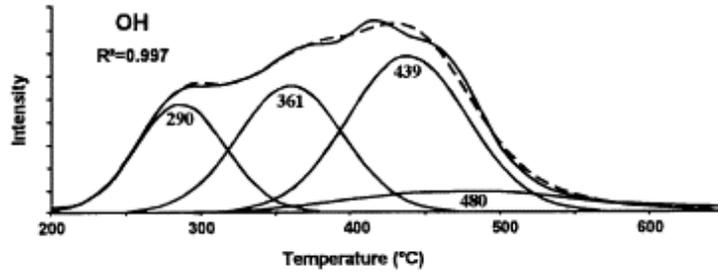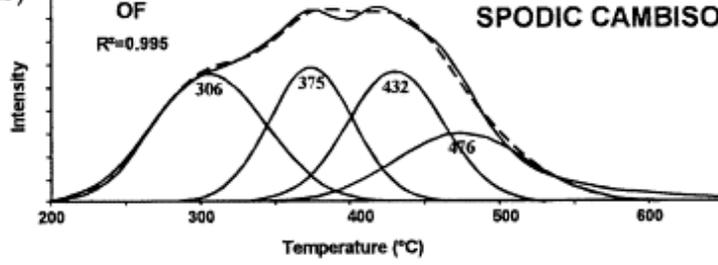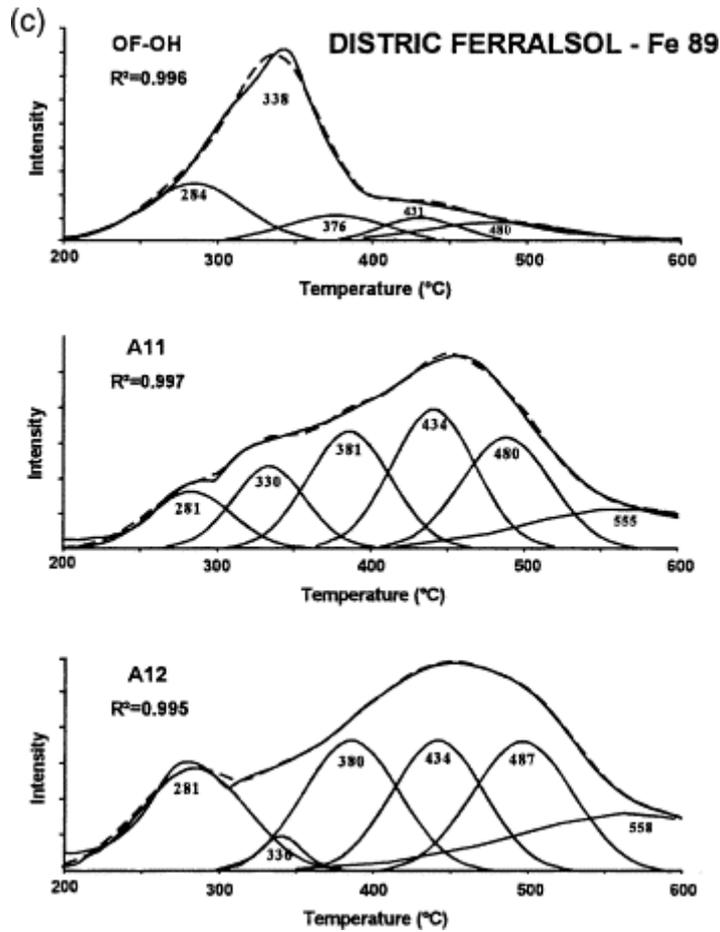
Fig. 10. Examples of pyrograms of soil samples from some of the studied profiles, with deconvolution of the multilobed S2 signals: 10a: podzol Po 39; 10b: spodic cambisol Cm 53; 10c: distric ferralsol Fe 89.
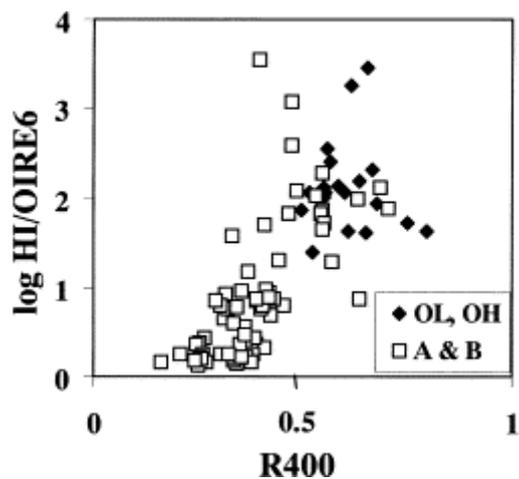
Fig. 11. R400 vs. log HI/OI diagram. R400 represents the proportion of the S2 signal integrated before 400 °C (T_{peak} equivalent pyrolysis temperature).

T_{max} values higher than 435 °C (i.e. T_{peak}>475 °C), which are sometimes observed in soils developed on sedimentary formations, and especially in the deepest horizons, are normally

caused by mature OM reworked from the substratum (Di-Giovanni et al., 1998, Di-Giovanni et al., 1999 and Di-Giovanni et al., 2000). Previous studies on coals and coaly materials provided evidence that the T_{max} values of such materials do not change in the course of weathering or only in the very latest stages when HI values were very low (Lo and Cardott, 1995). However, recent work shows that the invariance of T_{max} with increasing weathering only holds for weakly mature and mature materials, a marked Tmax increase with increasing alteration being observed for highly mature coals (starting equivalent vitrinite reflectance>1.5%: Disnar et al., 2001b and Copard et al., 2002). High T_{peak} values in SOM might also be caused by the presence of charcoals which have recently been judged responsible for Tpeak values of 500–600 °C found at about 1 m depth in laterite profiles in Brazil (Bodineau et al., 2002). The presence of such mature material admixed with variable amounts of recent organics, might also be responsible for the T_{peak} value of 513 °C given by the topsoil of a Columbian ferralsol. (sample 851; Table 1).

4. Conclusions

Rock-Eval pyrolysis rapidly provides essential information on the amount and composition of SOM. In addition to information on the abundance of SOM Rock-Eval pyrolysis provides insight into the composition of SOM and even into its structure. Compositional information relies on the hydrogen and the oxygen index (HI and OI) values, related to the H and O content of SOM, respectively. Structural information is less straightforward and relies on the shape of the S2 peak and on its "T_{peak}" value(s).

The present application of Rock-Eval pyrolysis to a large sample set shows that the method effectively allows one to follow the evolution of the humification process with increasing depth in soil profiles, i.e. the progressive disappearance of inherited biopolymers and the formation of humic substances. Other important features such as the extensive oxidation that usually affects SOM in podzols, are also clearly evidenced.

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