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Characterization of biogenic organic matter by stepwise thermogravimetry (STG)

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Key words: C:N ratio, combustion, muffle furnace, organic matter, STG, thermogravimetry

Abstract. The STG method presented here is a simple approach facilitating the characterization of biogenic organic materials. Pre-dried (130 °C) and grounded (< 0.5 mm) samples were heated in a muffle furnace at 280 °C for 6 h and subsequently at 520 °C for 6 h. The weight loss in the temperature range, 130–280 °C (PI) and 280–520 °C (PII), provided an index (Rp) defined as, Rp = PII/(PI + PII). Plant materials rich in structural carbohydrates generally showed a Rp index around 0.3, whereas Rp for animal tissues rich in proteins usually were around 0.6. A general relationship between Rp and C:N for living biogenic organic matter, ranging from leaves of terrestrial origin to marine invertebrate tissue, was described by the equation: $Rp = 0.791 \times (C:N)^{-0.246}$ ($n = 13$, $r^2 = 0.946$). During biological decomposition of composting barley straw, Rp increased from 0.17 to 0.37 and C:N decreased from 87 to 16. A similar Rp-C:N pattern was observed with depth in the upper 2 cm of an organic poor marine lagoon sediment (Rp increased from 0.43 to 0.47; C:N decreased from 8.4 to 7.7); indicating that microbial protein synthesis may have occurred with depth in this layer. The observed increase in both Rp and C:N with depth from 2 to 8 cm (Rp increased from 0.47 to 0.52; C:N increased from 7.7 to 10.3) suggested that humification may predominate in this zone. Accordingly, humic acids are found to have a Rp as high as 0.64. The Rp-C:N relationship appears to be a powerful two-dimensional tool applicable to characterize the bulk composition of various biogenic organic materials at different stages of decomposition.

Introduction

Biogenic organic matter of aquatic and terrestrial origin are generally mixtures of biopolymers such as carbohydrates, lipids, proteins, polyphenols (i.e. lignin) and less well characterized complex macromolecular humic substances (Parsons et al. 1961; Rice 1982; Mayer et al. 1986; Gadel & Bruchet 1987). The exact amount of each component contained in an organic complex is highly dependent on the origin of the material, i.e. whether it is plant or animal tissue from either aquatic or terrestrial sources, and on the actual stage of biological decomposition (Parsons et al. 1961; Käärik 1974; Rice 1982).

During the last decades a variety of chemical and physical methods have been applied for the analysis and characterization of organic matter at the

molecular level. These include: various extraction, oxidation and hydrolysis techniques (e.g. Parsons et al. 1961; Strickland & Parsons 1972; Rice 1982; Mayer et al. 1986; Hamilton & Hedges 1988); HPLC techniques (e.g. Lindroth & Mopper 1979; Jørgensen & Kristensen 1980); and combustion techniques such as ignition loss (e.g. Hedges & Stern 1984; Kristensen & Andersen 1987); elemental CHN analysis (e.g. Telek & Marshall 1974; Van Iperen & Helder, 1985; Kristensen & Andersen 1987); pyrolysis (e.g. Irwin 1979; Boon & Haverkamp 1982; Wilson et al. 1983; Whelan & Tarafa 1986; Gadel & Bruchet 1987); thermal analysis (e.g. Paterson & Swaffield 1981; Hirata & Werner 1987); and thermogravimetry (e.g. Tomassetti et al. 1986; Sheppard & Forgeron 1987). The composition of complex organic materials can usually be described precisely by combining several of these methods; however, no single analytical method exists, which is suitable to characterize the overall composition of organic matter.

Thermogravimetric analysis, i.e. recording of the weight loss of a sample subjected to an increase in temperature, is a technique generally used to study physical and chemical changes of materials as they are heated at a specific rate in a defined atmosphere (air, oxygen or nitrogen) (David 1975). Accordingly, thermogravimetry has been proposed as a method for fingerprinting polymeric organic mixtures (Sheppard & Forgeron 1987; Zimmermann et al. 1987).

Modern thermogravimetry, which involves expensive computer controlled analytical equipment, is most frequently used to study the thermal behaviour of minerals, fuels, and industrial plastic and rubber polymers (e.g. David 1975; Shafizadeh et al. 1976; Mehdi & Still 1985; Dollimore 1988). However, attempts to apply thermogravimetry for biological samples have been reported (e.g. Herrera et al. 1986; Tomassetti et al. 1986; Sheppard & Forgeron 1987; Zimmermann et al. 1987). Recently, Kristensen & Andersen (1987) have used a common muffle furnace to study the thermogravimetric behaviour of marine organic matter.

This study presents a simple and inexpensive method to characterize biogenic organic matter. Based on a two-step heating procedure, i.e. stepwise thermogravimetry (STG), organic matter from different sources are distinguished. The temperature intervals are selected such that the major weight loss peaks typically observed during heating are differentiated. A combination of STG and elemental CHN analysis is shown to provide a promising two-dimensional tool for use in ecological and biogeochemical studies on biological decomposition of biogenic organic matter.

Materials and methods

Samples

The thermal combustion characteristics of 26 different organic complexes, representing both aquatic and terrestrial environments, were examined. The materials were separated into four categories: 1. living biogenic; 2. compost; 3. detritus (sediment); 4. analytical grade (Table 1).

1. Living biogenic materials. A representative collection of 14 living animals, plants, and micro-organisms were used to describe the combustion characteristics of fresh, biologically undecomposed organic matter (Table 1, no. 1–14). The organisms examined were 3 species of marine invertebrates (no. 1 a polychaete; no. 3 a bivalve (only soft parts tested); and no. 7 a gastropod); 2 species of marine macroalgae (no. 4 a green and no. 9 a brown); 2 species of marine angiosperms (no. 8 and 10, seagrasses); 1 species of freshwater microalgae (no. 14, phytoplankton); 2 bacterial species (no. 5 and 6, from culture); egg white from chicken egg (no. 2); leaves from 2 species of mangrove trees (no. 11 and 13); and leaves from beech tree (no. 12). Sampling locations are indicated in Table 1. All organisms were sampled alive and dried at 100 °C for 12 h within 24 h after sampling. Phytoplankton and bacteria samples were pre-concentrated by centrifugation at 10 000 rpm for 30 min.

2. Compost. The influence of biological decomposition on thermal combustion characteristic of organic matter was examined using barley straw compost. Two batches of straw were used, one without (no. 15) and one with the addition of 25% livestock manure (barley:manure, 3:1; no. 16). The pre-chopped straw material (mean straw length: $\frac{1}{2}$–1 cm) was enriched with 1 g NaH_2PO_4 and 2 g $CaCO_3$ per liter substrate before the incubation. Two replicate series of both composts were incubated aerobically for 6 weeks under controlled conditions (water content: 80%; ambient temperature: 26 °C) in 1 liter jars. Each week samples were taken for thermal combustion, and elemental carbon (POC) and nitrogen (PON) analyses.

Humic acid (no. 17) was precipitated from 6 week old barley + manure compost (no. 16). Compost samples (0.5 g) was extracted anaerobically with 25 ml 0.1 M NaOH for 20 h. After centrifugation humic acids in the supernatant was precipitated with 6 M HCl (pH = 1) for 24 h. The humic acid residue was dried at 100 °C for 12 h.

3. Detritus. Thermal combustion of three detrital (i.e. sedimentary) materials

Table 1. A list of the organic materials used for the DTG and STG analyses. The Rp index, % organic carbon (POC) and C:N molar ratio are presented. The type and origin of the materials is indicated.

No.	Type	Rp	%POC	C:N	Origin
LIVING					
1	*Nereis diversicolor*	0.57	24.6	4.5	marine lagoon, Denmark
2	Egg white	0.56	48.4	4.2	chicken egg
3	*Cerastoderma* sp.	0.55	45.7	5.4	marine lagoon, Denmark
4	*Ulva lactuca*	0.52	34.3	7.1	marine lagoon, Denmark
5	*Escherichia coli*	0.50	43.3	4.9	laboratory culture
6	*Bacillus subtilis*	0.49	40.4	4.7	laboratory culture
7	*Hydrobia* spp.	0.43	19.2	10.8	marine lagoon, Denmark
8	*Ruppia maritima*	0.43	39.9	13.0	marine lagoon, Denmark
9	*Fucus vesiculosus*	0.37	46.6	21.5	marine lagoon, Denmark
10	*Zostera marina*	0.39	36.5	25.6	marine lagoon, Denmark
11	*Avicennia marina*-leaves	0.33	46.5	31.6	mangrove swamp, Thailand
12	*Fagus silvatica*-leaves	0.32	40.0	33.6	beech forest, Denmark
13	*Rhizophora apiculata*-leaves	0.29	45.1	51.3	mangrove swamp, Thailand
14	*Chlorella* sp.	nd	nd	nd	pond, Denmark
COMPOST					
15	Barley straw	0.17	44.6	83.6	harvest, Denmark
16	Barley-manure	0.25	39.1	26.6	75% straw + 25% livestock manure
17	Humic acid	0.64	45.4	19.6	NaOH extract of no. 16
DETRITUS					
18	Mangrove detritus	0.42	25.3	50.2	mangrove swamp, Thailand
19	Mangrove sediment, 0–1 cm	0.56	2.3	29.3	mangrove swamp, Thailand
20	Estuarine sediment, 0–5 cm	0.43	6.6	11.4	Kolding Fjord, Denmark
21	Marine sediment, 0–0.5 cm	0.44	0.3	8.4	marine lagoon, Denmark

PURE					
22	Glutamic acid	0.48	41.9	5.2	analytical grade
23	Glucose	0.36	40.5	–	analytical grade
24	Cellulose	0.24	40.2	–	analytical grade
25	Sawdust	0.31	50.7	–	pine-wood
26	Mixture	0.35	45.6	39.9	50% sawdust, 35% glucose, 15% glutamic acid

nd = not determined

No STG and C:N analysis was performed on material, No. 14, but a DTG30 analysis is shown in Fig. 1.

Table 2. Carbohydrate, lignin, lipid, and protein content of materials similar to those examined for thermal decomposition characteristics in this study.

Material	Carbohydrate	Lignin	Lipid	Protein	Ref
Polychaeta	4.8	0	9.0	78.5 (80.3)	[1]
Egg white	~0	0	0.4	90.3 (88.4)	[2]
Bivalvia	20.0	0	4.0	71.1 (72.6)	[1]
Ulva lactuca	77.0	0	0.1	22.7 (49.0)	[3]
Bacteria	16.6	0	9.4	52.4 (73.9)	[4]
Fucus vesiculosus	90.7	~0	2.6	6.6 (20.0)	[3]
Aquatic angiosperm	81.5		2.1	16.1 (20.3)	[5]
Tree-leaves	77.1	12.5	2.9	6.7 (9.7)	[5]
Chlorella sp.	33.4	0	16.1	46.4 (nd)	[6]
Cellulose	100.0	0	0	0 (0)	-
Pine-sawdust	71.7	26.7	1.5	~0 (0)	[7, 8]
Barley straw	82.6	13.6	1.0	1.0 (3.7)	[9]

References: [1] Nicol (1967); [2] Long (1964); [3] Chapman (1970); [4] Fenchel & Blackburn (1979); [5] Lieth (1975); [6] Morowitz (1968); [7] Käärik (1974); [8] Koch (1985); [9] Lynch (1979)

The values for each individual compound are given in % of the ash free dry weight. Values in brackets are the estimated protein content, based on the presently measured N content × 6.25 (nd = not determined).

were examined. Peat-like mangrove detritus, which was washed up on the high tide line, was collected in the Ao Nam Bor mangrove swamp, Thailand (no. 18). Simultaneously, the upper sediment layer (0–1 cm) within the mangrove forest was sampled (no. 19) (for details, see Kristensen et al. 1988). A 8 cm vertical profile (0–0.5 (no. 21), 0.5–1, 1–2, 2–3, 3–4, 4–6, 6–8 cm) was sampled in the organic poor sediment of the shallow marine lagoon Fællestrand, Funen, Denmark (for details, see Kristensen, in prep). The top 5 cm sediment layer was sampled in the organic rich estuary Kolding Fjord, Denmark at 5 m water depth (no. 20).

4. Analytical grade materials. The thermal characteristics of 3 pure compounds: glutamic acid (no. 22); glucose (no. 23); and cellulose (no. 24) were examined. Additionally, sawdust from pine-wood (no. 25) was compared with pure cellulose to evaluate the role of lignin on the thermal combustion pattern (pine-sawdust contains ~27% lignin by weight, Table 2). The potential role of heat induced chemical interactions between individual components of a mixture during thermal combustion was examined using a mixture of 50% sawdust, 35% glucose and 15% glutamic acid (no. 26).

Sample preparation

All samples were dried at 100 °C for 12 h, cooled in a dessicator for at least 2 h, and ground with a mortar and pestle. Only materials with a particle size less than 0.5 mm were used. Duplicate samples (0.5 to 1.5 g) were placed in pre-weighed crucibles. Weights of the 100 °C dried samples and all subsequent weights were determined to the nearest 0.1 mg on a mettler H45 balance.

Procedures

DTG30. Samples used for differential 30 °C-step thermogravimetry (DTG30) and stepwise thermogravimetry (STG) in air were heated to the chosen temperatures in a Hereaus MR 170 muffle furnace. Temperature was monitored by a 13% Pt/Pt-Rh thermocouple and recorded on an Olivetti M240 personal computer (PC). The PC controlled both steady state temperature (within a range of ± 2 °C) and combustion time via interface to the furnace. The chosen steady state temperatures was reached within 0.5 h after the start and the combustion was terminated by the PC at the selected time.

During DTG30, the 100 °C dried samples (in duplicates or triplicates) were heated to 130 °C for 4 h, cooled in a dessicator for at least 2 h, weighed to the nearest 0.1 mg and returned to the muffle furnace at 160 °C for 4 h, cooled in a dessicator for at least 2 h, weighted, etc. This was continued in steps of 30 °C until 520 °C.

DTG. Continuous differential thermogravimetry (DTG) on ground samples (particles < 0.5 mm) were analysed with a Mettler TA 3000 Thermal Analysis System at temperatures from 100 to 600 °C in a stream of atmospheric air. All samples were dried in the Mettler furnace at 100 °C for 10 min prior to testing. Heating rate was 20 °C per min. Sample size was on average about 30 mg. The data analysis system plotted weight loss and the first derivative (DTG) as a function of temperature. Samples no. 4, 5, 6, and 10 were analysed. Only no. 4 and 10 are presented here.

STG. Stepwise thermogravimetry was performed as a two step combustion, i.e. the 130 °C predried samples (in duplicates) were heated at two temperatures in a muffle furnace: at 280 °C for 6 h, and at 520 °C for 6 h. The samples were weighed after each step and subsamples were taken for elemental carbon (POC) and nitrogen (PON) analyses.

POC and PON. Analysis of particulate organic carbon (POC) and nitrogen

(PON) were performed in duplicates on 5–10 mg subsamples with a Hewlett-Packard 185B CHN-analyzer and recorded on a Hewlett-Packard 3380A integrator.

Results

Differential thermogravimetry (DTG30 and DTG)

The DTG30 combustion pattern for the materials tested (material no. 2, 4, 10, 11, 13, 14, 18, 22, 23, 24, 25, 26; Fig. 1; Table 1) appeared to be either bimodal or trimodal. The weight loss per 30 °C step was generally highest in the range 160 to 280 °C (peak I, max. 10–42%). A trough around 280 to 340 °C and a subsequent second weight loss peak in the range 340 to 490 °C was evident for all materials (peak II, max. 4–22%). Samples containing analytical grade low molecular compounds (no. 22, 23 and 26), however, exhibited a trimodal weight loss with a significant peak around 130 to 190 °C (peak 0, max. 9–18%). The precision of replicates at each temperature interval were usually within $\pm$ 10% of the mean. The modal temperature of the two major peaks (I and II) varied from 175 °C (*Ulva lactuca*, no. 4) to 265 °C (glucose, no. 23) for peak I and from 325 °C (sawdust, no. 25) to 445 °C (egg white, no. 2) for peak II.

The comparison of DTG30 and DTG for *Zostera marina* and *Ulva lactuca* shown in Fig. 2, reveal that the DTG peaks generally were located at temperatures ca. 60 °C higher than the DTG30 peaks (except for the *Zostera marina* peak II). The overall thermal combustion pattern, on the other hand, appeared similar by both methods, indicating the applicability of the discrete DTG30 method for thermogravimetric analysis.

Stepwise thermogravimetry (STG)

The DTG30 procedure is time consuming and tedious when a large number of samples are to be analysed. A promising alternative is to apply stepwise thermogravimetry (STG), i.e. weight loss determination of dried samples after combustion at two successive temperatures:
— at the trough between peak I and peak II;
— at the trough between peak II and the inorganic carbonate peak.

Combustion parameters
Loss of organic carbon and nitrogen by volatilization using a 130° drying temperature appeared to be negligible in the present study, although a 2 to

10% weight loss was observed between 100 and 130 °C. The organic carbon and nitrogen content of samples dried at 100 °C for 12 h (POC_{est} and PON_{est}), converted to 130 °C using the weight loss found from 100 to 130 °C was related to the actually observed organic carbon and nitrogen content in samples after heating at 130 °C for 6 h (POC_{obs} and PON_{obs}) according to:

$$POC_{est} = 0.996POC_{obs} - 0.206, \quad r^2 = 0.997, \quad n = 17$$

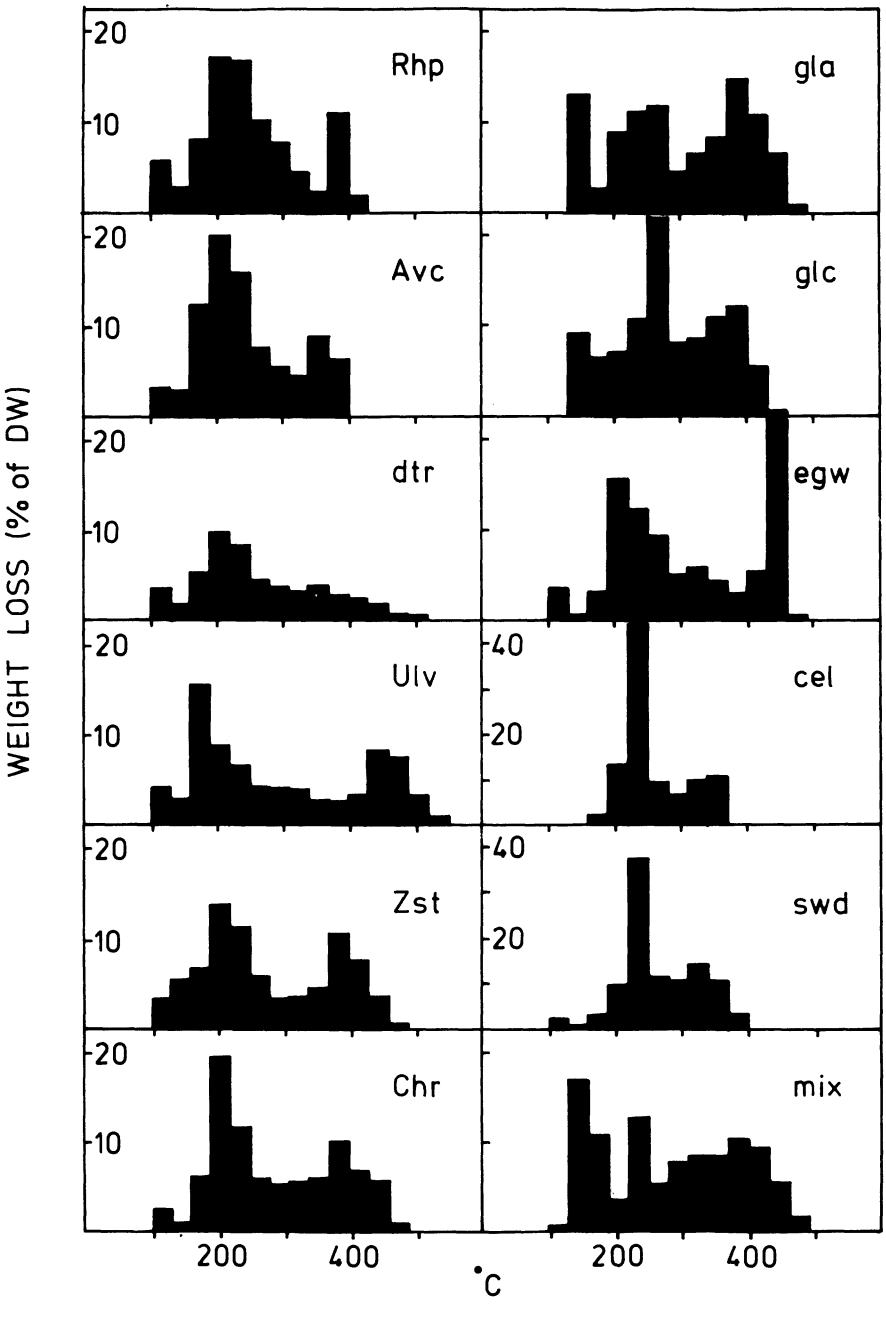
$$PON_{est} = 0.954PON_{obs} - 0.178, \quad r^2 = 0.993, \quad n = 11$$

Regression coefficients for both elements are not significantly different from 1.0, indicating that no measurable loss of carbon or nitrogen occurred during heating at 130° for 12 h.

The intermediate combustion temperature for STG was tested using *Ulva lactuca* (no. 4), *Zostera marina* (no. 10) and estuarine sediment (no. 20). The two step STG combustion procedure was found to alter the thermal combustion pattern of organic matter compared to DTG30. The direction of changes in combustion temperature was similar to that observed between DTG30 and DTG (Fig. 2). The exact position of the trough in STG, and thereby the most appropriate intermediate combustion temperature was found to be around 280 °C for the materials tested.

The upper combustion temperature has previously been established by Kristensen & Andersen (1987) to be situated as the 520 °C trough between the organic matter weight loss peaks and the $CaCO_3$ weight loss peak.

Combustion time needed to provide reproducible STG results was tested using 4 duplicate samples of *Fagus silvatica* leaves (no. 12), *Rhizophora apiculata* leaves (no. 13) and mangrove sediment (no. 19). A progressive weight loss occurred with time (2–12 h) in the temperature range 130 to 280 °C, accompanied by a decrease in the range 280 to 520 °C. The excess weight loss or tailing observed at 280 °C when combusted for 8 h compared to 6 h only accounted for 1.1 to 3.2% of the total 6 h weight loss observed at 520 °C. Since the non steady state tailing continued beyond 8 h in all of the tested materials, practical reasons decided that the 6 h combustion time was chosen in this study. By this approach, though, it is important that the combustion at 280 °C is terminated precisely 6 h after the start to avoid errors due to uncontrolled loss of material. The precision of replicates after a 6 h combustion at 280 °C was usually within $\pm 1\%$ of the mean.


WEIGHT LOSS (% of DW)
Rhp
gla
Avc
glc
dtr
egw
Ulv
cel
Zst
swd
Chr
mix
20
10
40
200
400
°C

The Rp index

A quantitative measure based on the STG method was applied using the Rp index, defined as:

$$Rp = PII/(PI + PII)$$

Where PI is Peak I: weight loss of samples heated in the temperature range 130–280 °C for 6 h, and PII is Peak II: weight loss of the same samples heated in the temperature range 280–520 °C for 6 h. The Rp index, therefore, represents the fraction of total combustible organic matter which was lost in the high temperature range (PII). Rp values for the materials used in this study are presented in Table 1. The precision of replicates were usually within $\pm 1\%$ of the mean for Rp.

A comparison of Rp values estimated from both DTG30 and STG combustion procedures on samples no. 2, 4, 10, 11, 13, 18, 24, and 25 revealed highest Rp values for STG. However, the difference between the two methods appeared to be constant within the range of materials tested as indicated by a regression coefficient close to 1: (STG) = 1.04 (DTG30) + 0.05, $r^2 = 0.922$, n = 8. Less material was evidently combusted at low temperatures (peak I) when STG was used compared to DTG30 (intercept = 0.05). This difference may be a consequence of the previously mentioned non steady state combustion time used in the STG method.

C:N ratio

The carbon content and C:N ratio of the materials tested, based on elemental carbon (% POC) and nitrogen analysis (% PON), are given in Table 1. The precision of replicate carbon and nitrogen analysis were usually within $\pm 7\%$ of the mean. Protein content of the examined biogenic materials, estimated as % PON × 6.25, is shown in Table 2 together with published carbohydrate, lignin, lipid and protein data of similar materials.

←

Fig. 1. The DTG30 combustion pattern from 100 to 520° of 12 organic materials: Rhp, *Rhizophora apiculata* leaves (no. 13); Avc, *Avicennia marina* leaves (no. 11); dtr, mangrove detritus (no. 18); Ulv, *Ulva lactuca* (no. 4); Zst, *Zostera marina* (no. 10); Chr, *Chlorella* sp. (no. 14); gla, glutamic acid (no. 22); glc, glucose (no. 23); egw, egg white (no. 2); cel, cellulose (no. 24); swd, sawdust (no. 25); and mix, a mixture of 50% sawdust, 35% glucose, and 15% glutamic acid (no. 26). The values are given as % loss of dry weight for each 30° interval. The same samples of each material were used throughout the combustion procedure. Note the different scaling for cel and swd.

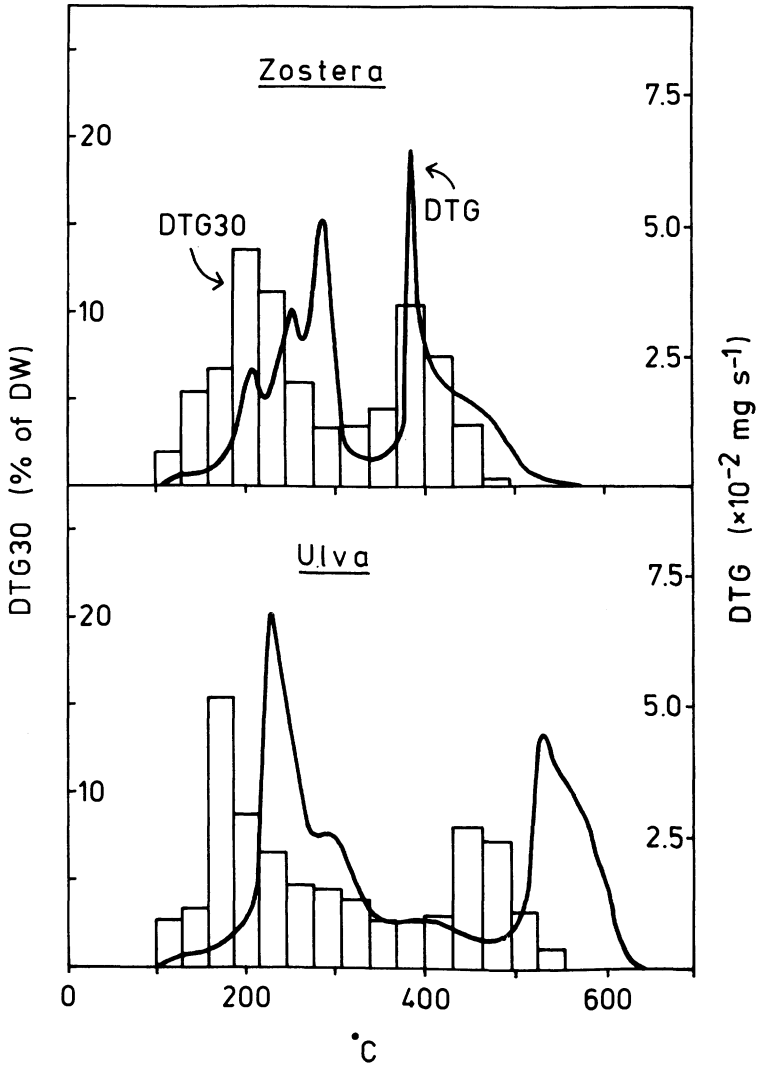


Fig. 2. Comparison of DTG30 and continuous DTG (heating rate 20° min^{-1}) on *Zostera marina* and *Ulva lactuca* in the range from 100 to 650 °C. Values of DTG30 are presented as % loss of dry weight for each 30° interval. DTG values are presented as weight loss in 10^{-2} mg s^{-1}.

Discussion

Combustion pattern

The bimodal or trimodal combustion patterns found by the DTG30 method (Fig. 1) are similar to previously observed patterns for biogenic materials

using either continuous differential thermogravimetry (DTG) or differential thermal analysis (Paterson & Swaffield 1981; Tomassetti et al. 1986; Herrera et al. 1986; Sheppard & Forgeron 1987; Zimmermann et al. 1987). In agreement with the present study (Fig. 2) published DTG data usually show peaks at significantly higher temperatures than found by the DTG30 method.

It is generally accepted that the thermal combustion of organic matter in an O_2 atmosphere occur in two main sequences (Shafizadeh & Fu 1973; David 1975; Morgan & Smith 1978; Whelan & Tarafa 1986; Sheppard & Forgeron 1987):

— Low DTG temperature region (100 to 350 °C, equivalent to PI in STG): evaporation (i.e. dehydration of hydroxylated aliphatic structures, decarboxylation of acid groups and generation of low molecular weight volatile compounds); oxidative degradation of aliphatic carbohydrates; random chain-scission of weak bonds; crosslinking and peroxide formation; formation of compounds of less ordered structure; cyclization; and formation of carbonaceous char.

— High DTG temperature region (350 to 600 °C, equivalent to PII in STG): oxidation of aromatic groups (polyphenolic compounds like lignin, humic substances and kerogens) and char.

In general, aromatic compounds are thermally much more stable than aliphatic (David 1975). The actual chemical composition, e.g. the relative content of cellulose, lignin, protein and humic compounds, of biogenic mixtures may have significant influence on the overall thermal combustion pattern.

Plant materials rich in structural carbohydrates (Fig. 1: no. 13, 11, 24, 25; Table 2) appear to be combusted at relatively low temperatures, i.e. most material, such as celluloses, is lost below 310 °C (DTG30, peak I), generally leaving 25–30% of the dry weight, e.g. lignins, to be combusted at higher temperatures (DTG30, peak II). The combustion is usually terminated around 400 °C. Herrera et al. (1986) found, by DTG, that the major percentage weight loss of hemicelluloses and celluloses occur at the low temperature range between 200 and 350 °C, whereas lignin combustion is confined to higher temperatures, i.e. between 300 and 500 °C. Phenols, the pyrolysis products of lignin, are known to be absent during pyrolysis in a nitrogen atmosphere at temperatures below 300 °C (Morgan & Smith 1978). Some overlap apparently occurs between cellulose and lignin during the DTG30 combustion process. This is evident from the observed similarity in combustion patterns of pure cellulose (no lignin) and pine sawdust ($\sim$ 27% lignin; Table 2; Fig. 1). The lignin content is, however, responsible for a larger peak II (26%) for pine sawdust. The presence of a peak II (20%) for

Table 3. The C:N ratio of peak I (130–280 °C) and peak II (280–520 °C) for various materials. The overall value ($\bar{x}$) is presented.

No.	Material	Peak I	Peak II	$\bar{x}$
2	Egg white	5.6	3.6	4.4
4	*Ulva lactuca*	30.0	8.4	15.9
10	*Zostera marina*	75.5	17.7	34.9
11	*Avicennia*-leaves	34.1	11.0	25.0
13	*Rhizophora*-leaves	86.0	16.2	48.1
18	Mangrove detritus	40.7	13.3	34.4
20	Estuarine sediment	26.4	5.3	12.5

pure cellulose is probably caused by oxidation of char which is formed during pyrolysis and oxidation of the cellulose molecules at temperatures below 300 °C.

Protein rich marine plant and animal tissues (Fig. 1: no. 4, 10, 14, 2; Table 2), on the other hand, retain about half or more of the organic matter to be combusted at high temperatures (DTG30, peak II). The well defined second peak is usually terminated at temperatures around 500 °C. The general role of proteinaceous materials on thermal combustion is not well established (Zimmermann et al. 1987). However, protein-like amine or amide polymers are known to be combusted at higher temperatures than non-nitrogen aliphatic polymers (David 1975; Mehdi & Still 1985). The presence of a very high DTG30 peak II for egg white (Fig. 1) confirms that a major fraction of proteinaceous compounds are thermally stable at very high temperatures. Similarly, the nitrogen content of the peak II material is generally 2–7 times higher than that of peak I (Table 3). This indicates that nucleation and cyclization processes involving nitrogen components of proteinaceous materials may occur at temperatures below 300 °C, thereby producing thermally stable nitrogen rich (char-like) residues. The thermal stability may partly be caused by the fact that double and triple carbon-nitrogen bonds are stronger than their carbon-carbon counterparts (Morowitz 1968).

The combustion characteristics of lipids, which usually account for less than 10% by weight of biogenic materials (Table 2), has not been emphasized experimentally in the present study. Evidence suggests, however, that the general combustion pattern of lipids is similar to that of aliphatic carbohydrates. Thus Varma & Singh (1980) reported a 75–80% weight loss during DTG of soaps (oleate, laurate, caprate and caprylate) at temperatures up to 360°, followed by a 10–20% loss between 360 and 500°. The first peak corresponds to the evolution of ketones and volatile hydrocarbons due to chain scission and oxidation, whereas the second peak represents

carbon dioxide loss from char oxidation. Accordingly, lipids and aliphatic carbohydrates appear indistinguishable by conventional thermogravimetric methods.

Free (volatile) low molecular compounds, e.g. fatty acids, may evaporate from organic matter at relatively low temperatures (i.e. below 150°) (Morita 1957; Schnitzer et al. 1964; Lawson & Pemberton 1965; Kodama & Schnitzer 1969; Johnson 1977; Zimmermann 1987). However, no measurable loss of organic carbon and nitrogen occurred in the present study using a 130 °C drying temperature. This is in accordance with the generally low (< 1%) content of volatile compounds in biogenic materials (Long 1964). The actual weight loss observed by DTG30 up to 130 °C is more likely caused by loss of residual moisture (or lattice bound water) (Tomassetti & Campanella 1986; Zimmermann 1987). Therefore, no serious errors are introduced by using a 130 °C drying temperature instead of 100 °C. In fact, the common use of 100 °C as drying temperature may overestimate the dry weight of biogenic materials by up to 10% due to bound residual moisture.

The peak 0 evolving during the DTG30 combustion of glutamic acid (no. 22) and glucose (no. 23) between 130 and 190 °C (Fig. 1) is probably caused by a rapid dehydration of hydroxy functional groups in these low molecular materials (Shafizadeh et al. 1976; Pavlath & Gregorski, 1985). A similar loss is usually not found during thermal combustion of biogenic materials (Fig. 1). The concentration of free, low molecular compounds, like amino acids and monosaccharides, are usually low in these polymeric mixtures (Long 1964; Parsons et al. 1984).

When compounds of known thermal behaviour are mixed, peak shifts during combustion have been observed (Smothers & Chiang 1958; Sandermann & Augustin 1963; Zimmermann et al. 1987). Some compounds may act as catalysts accelerating the reactions and lowering the temperature where combustion occurs. In the present study the DTG30 combustion pattern of an artificial mixture (Fig. 1, no. 26) is almost the integrated result of its individual components. However, the dehydration peak (peak 0) found below 190 °C accounts for a much higher proportion of the total weight loss than estimated by simple addition of the individual components. The "cellulose" peak from sawdust is clearly evident in the mix, as well as the massive peak II derived from glutamic acid and glucose. Although the specific combustion pattern of each compound is diffiult to isolate in mixtures, the overall fingerprint may be useful in the characterization of a complex biogenic material and may suggest directions for further chemical analysis.

Relationship between the Rp index and C:N ratio

The Rp index provides information on the overall chemical composition of organic matter, i.e. the proportions of various compounds, such as carbohydrates, lignin, proteins and humic substances. Similar approaches, although with different purposes, have previously been introduced in thermal pyrolysis and DTG studies (Morgan & Smith 1978; Whelan & Tarafa 1986; Sheppard & Forgeron 1987). Low Rp values (0.2–0.3) indicate materials composed mainly of carbohydrates (plants), whereas high Rp values (0.4–0.7) indicate high concentrations of lignin (plants), proteins (plants and animals) and humic compounds (sedimentary detritus) (Table 1).

The nitrogen content or C:N ratio has been widely used in ecological studies to describe the chemical composition (i.e. protein content) and nutritional value of biogenic organic matter (Redfield et al. 1963; Harrison & Mann 1975; Blackburn & Henriksen 1983; Lancelot & Billen 1985; Kristensen & Blackburn 1987). Generally, the C:N ratio provides valuable information on the elemental composition of organic matter, but it appears relatively insensitive to many of the changes (e.g. humification) that occur during biological decomposition of organic matter (Odum et al. 1979; Rice 1982: Hylleberg & Riis-Vestergaard 1984; Lancelot & Billen 1985).

By combining the C:N ratio with the Rp index a more detailed description of the overall composition of biogenic organic matter can be obtained. The Rp-C:N relationship for 13 living biogenic materials, which is presented in Fig. 3, can be described by:

$$Rp = 0.791 \times (C{:}N)^{-0.246} \quad (1)$$

or:

$$(C{:}N) = 0.385 \times Rp^{-4.065} \quad (2)$$

where $r^2 = 0.946$. Equations (1) and (2) indicate a general negative logarithmic relationship between C:N and Rp for fresh, undecomposed organic matter, irrespective of the origin: marine, limnic or terrestrial; and level of organization: bacteria, algae, plants, animals. Low C:N and high Rp are typical for animal tissues rich in proteins, whereas high C:N and low Rp represent terrestrial plants rich in structural carbohydrates. The inverse Rp-C:N relationship, therefore, provides a highly sensitive two-dimensional characterization of organic matter. Nitrogen rich organic matter of different origin, e.g. bacteria and animal tissue, is almost indistinguishable using the

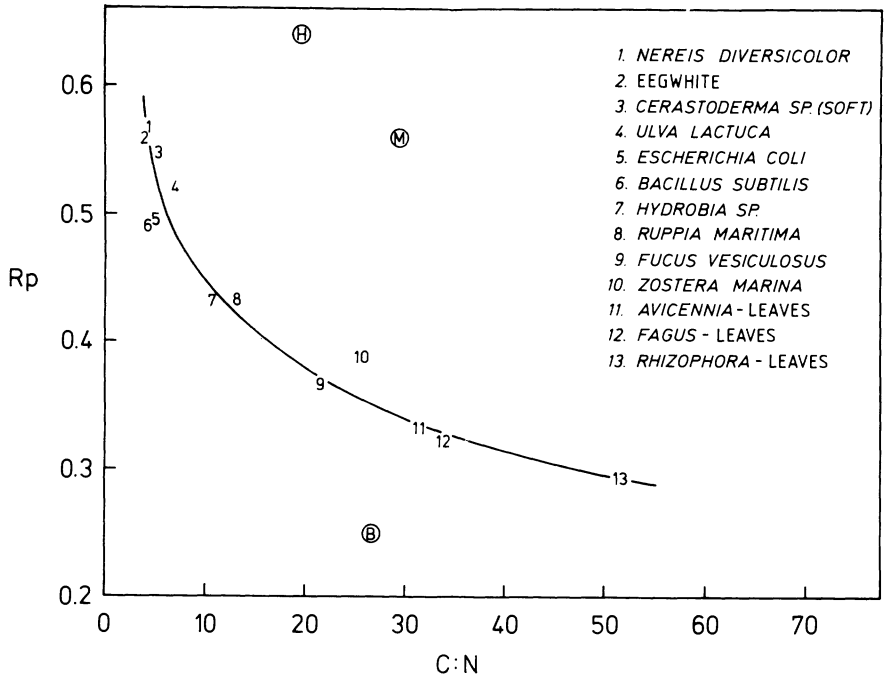


Fig. 3. The relationship between Rp index and C:N ratio for 13 different living biological materials (1–13). The position of fresh barley straw + manure (B), humic acid (H), and mangrove sediment (M) are shown for comparison. The exact figures can be obtained from Table 1.

C:N ratio. However, when the Rp-C:N relationship is applied a clear separation is evident: *E. coli* (no. 5) – 0.50, 4.9; and *Nereis diversicolor* (no. 1) – 0.57, 4.5 (Fig. 3). The difference in chemical composition, which is indicated by Rp, is probably caused by the presence of high concentrations of nitrogen rich nucleic acids in bacteria (Fenchel & Blackburn 1979). Variations in protein content of carbohydrate rich plant materials, on the other hand, is poorly described by Rp alone. However, when the background nitrogen level is low, the C:N ratio becomes a very sensitive indicator, e.g. *Avicennia marina* leaves (no. 11) – 0.33, 31.6: and *Rhizophora apiculata* leaves (no. 13) – 0.29, 51.3. In addition, the Rp-C:N relationship (eq. (1) and eq. (2)) may provide rough estimates of C:N ratios by extrapolation from Rp values, and vice versa. By doing so, however, care should be taken to assure that the samples tested are fresh biological materials, since partly decayed organic matter may deviate significantly from the idealized relationship (Fig. 3). Furthermore, sediments rich in clay may exhibit erronously high Rp values due to a significant loss of structural water at temperatures between 400 and 500 °C (Mook & Hoskin 1982).

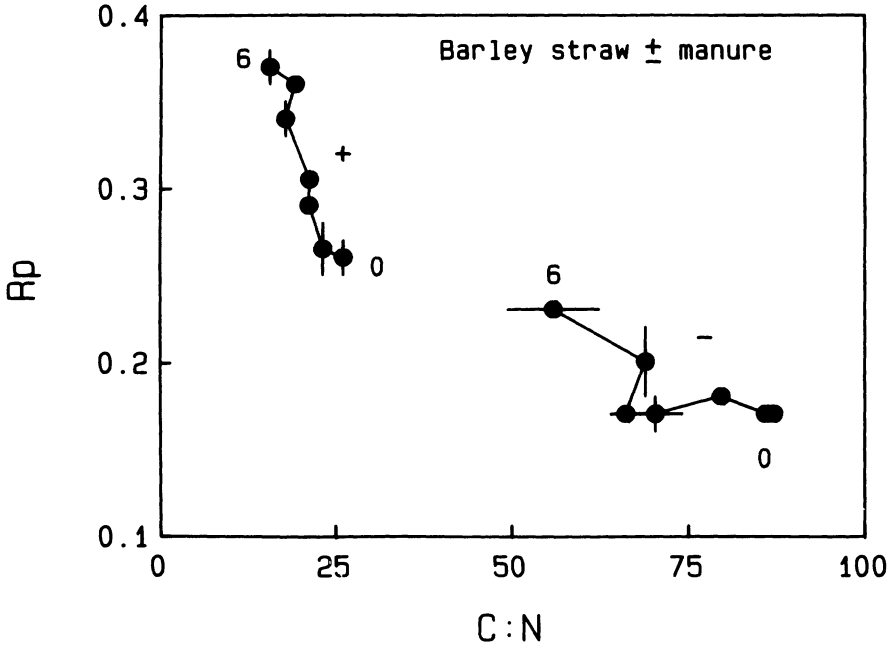


Fig. 4. The relationship between Rp index and C:N ratio during a 6 week aerobic decomposition period for barley straw without (−) and with (+) addition of 25% livestock manure. Each symbol represents mean of 2 weekly samples. The temporal decomposition pattern of both composts are indicated by 0 (start samples) and 6 (week 6 samples). Error bars represent range of 2 replicates.

The Rp-C:N relationship probably has its most important use in studies on biological decomposition of organic matter. Figures 4 and 5 show the Rp-C:N relationship and the DTG30 combustion pattern, respectively, of barley straw ± manure addition during a 6 week decomposition period. Carbon and nitrogen loss during the incubation period is 11.24 mmol C $g\,dw^{-1}$ and ~0 mmol N $g\,dw^{-1}$ without, and 11.55 mmol C $g\,dw^{-1}$ and 0.24 mmol N $g\,dw^{-1}$ with manure addition. Growth of bacteria during the initial decomposition of the most labile carbohydrate constituents of the nitrogen poor barley straw is accompanied by assimilation (or immobilization) of available nitrogen compounds. A similar decrease of the C:N ratio and even an absolute nitrogen enrichment of the particulate material has often been reported during the course of nitrogen deficient macrophyte detritus decomposition in microcosms (Harrison & Mann 1975; Rice & Tenore 1981; Lancelot & Billen 1985). The decrease in C:N from 87 to 56 in pure barley straw compost suggests a build-up of microbial proteins and amino sugars. The slight increase in Rp from 0.17 to 0.23, indicates that such protein enrichment, although large relatively, is low in absolute amounts. When

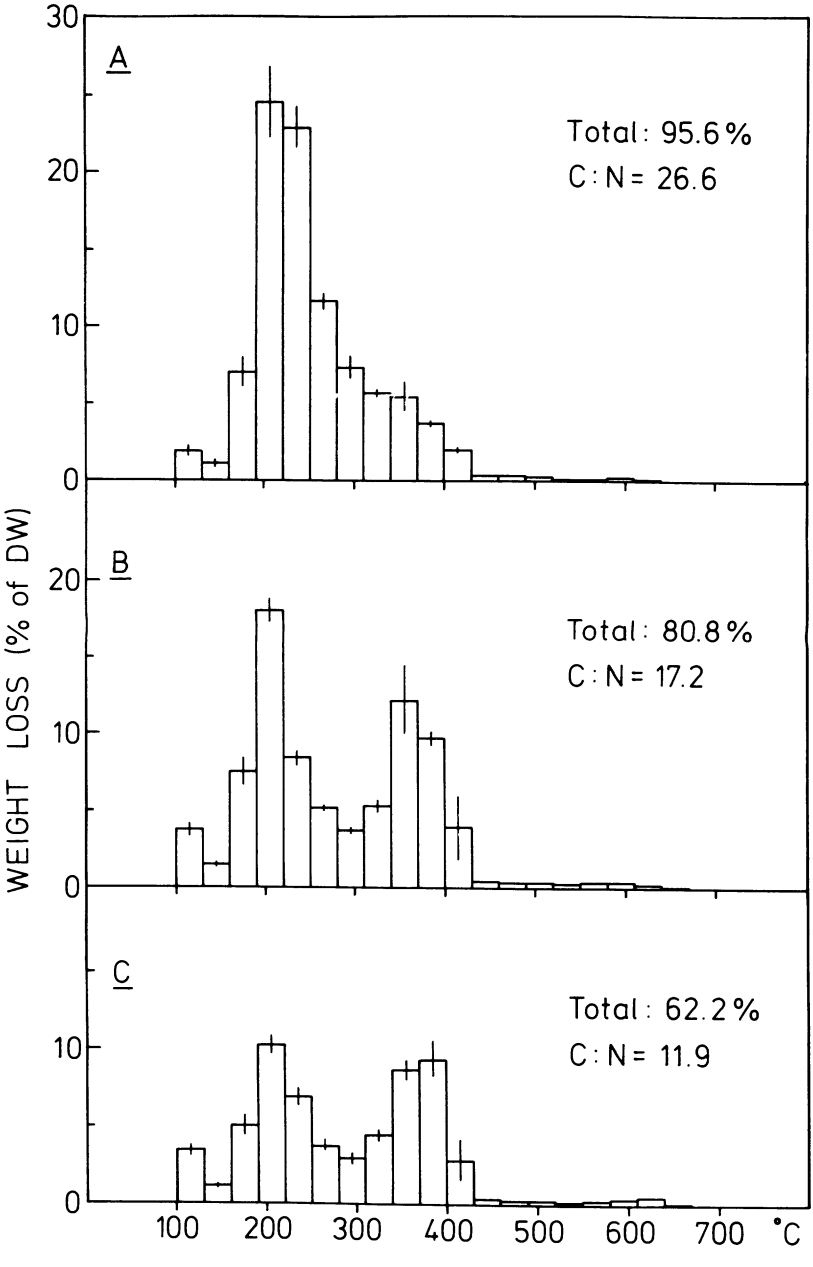


Fig. 5. DTG30 combustion pattern of barley straw with manure addition. (A) at the start of the decomposition period; (B) after 2.5 weeks; and (C) after 5 weeks decomposition. "Total" indicate the total weight loss on ignition at 520 °C, and "C:N" indicate the C:N ratio of 100 °C dried start material. Error bars represent range of 2 replicates.

nitrogen rich manure is added the change in C:N during straw decomposition is less pronounced (from 26 to 16). But due to microbial decomposition products Rp increases significantly (from 0.26 to 0.37). The overall Rp-C:N pattern of decaying barley straw (Fig. 4) has a striking resemblance with that of living biological materials (Fig. 3), suggesting that production of microbial tissue is a major determinant for the Rp-C:N relationship. Not all of the microbial produced organic nitrogen is in the form of protein but rather in the form of amino-sugar derivatives, cell wall remains and non-labile humic compounds (Lancelot & Billen 1985). Thus, an extrapolation of protein content from total nitrogen may overestimate the true protein content of sedimentary detritus by more than 50% (Table 2; Odum et al. 1979; Harrison & Mann 1975). The observed Rp-C:N value of 0.64, 19.6 for humic acid extracted from decomposed barley straw (Table 1) indicates the presence of nitrogen containing aromatic complexes. A significant fraction of this humic nitrogen may, however, be of proteinaceous origin, since the relatively non-specific NaOH extraction employed is likely to retrieve proteins as well as humic acid (Odum et al. 1979). During late stages of decomposition, detritus generally becomes richer in reactive phenolic and carbohydrate groups which may form condensation products with amino acids, yielding precursors to complex nitrogenous humic geopolymers (Rice 1982). Thus, if the present decomposition process was allowed to proceed for extended time periods (i.e. beyond 6 weeks), both Rp and C:N is expected to increase due to nitrogen remineralization and humification. Such C:N increase has previously been observed at the end of the decomposition process for aquatic macrophytes (Rice & Tenore 1981). The humification process may continue gradually until all carbon eventually is fixed into humic geopolymers, leading to Rp-C:N close to that of pure humic acid.

The Rp-C:N depth pattern found in the marine Fællesstrand sediment may indicate a successive decomposition of detritus (Fig. 6). The sandy, low organic sediment in the Fællesstrand lagoon is characterized by a very high benthic primary production (mostly diatoms, $> 200\,g\,C\,m^{-2}\,yr^{-1}$) (Kristensen, in prep.). The organic content decreases from 0.3% C at the surface to 0.1% C at 6–8 cm depth, with the steepest decrease in the most biological active zone from 0 to 3 cm. The increase in Rp and decrease in C:N occurring from 0 to 2 cm may result from microbial and meiofaunal growth (protein synthesis) during decomposition of newly produced organic matter. Thus, bacteria and animals generally exhibit higher Rp and lower C:N than algae (Table 1). Below 2 cm both Rp and C:N increases, suggesting protein mineralization and humus formation. Proteins, which usually account for less than 20% of the organic matter in sediments, are known to decrease

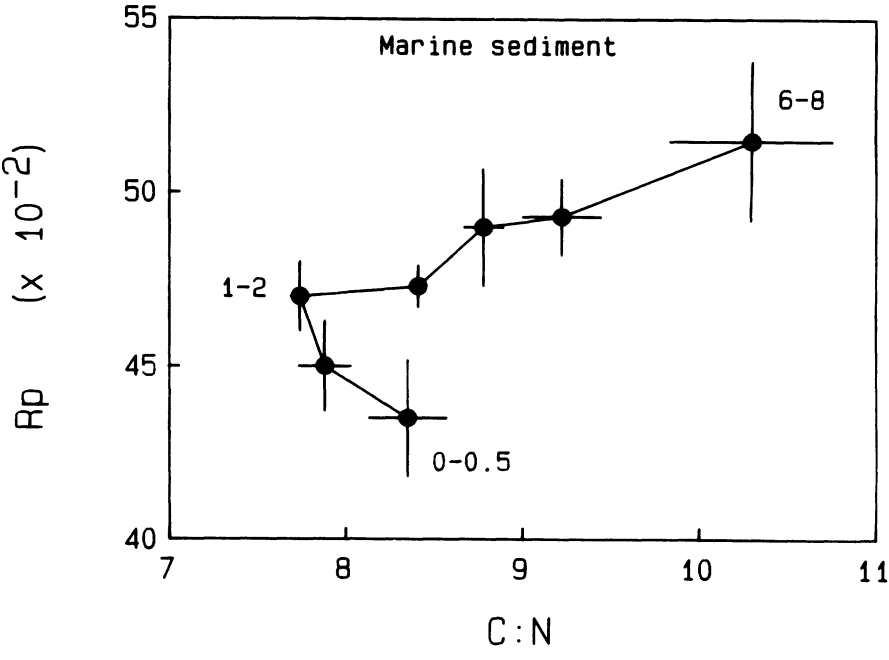


Fig. 6. The relationship between Rp index and C:N ratio in a vertical sediment profile from the marine lagoon Fællesstrand, Denmark. Depth intervals, 0–0.5, 1–2, and 6–8 cm, are indicated. Error bars represent S.D. of 4 replicates.

substantially with increasing depth (Hylleberg & Riis-Vestergaard 1984; Mayer et al. 1986). Humic compounds, on the other hand, are reported to account for up to 60% of the organic matter at depth in marine sediments (Brown et al. 1972; Nissenbaum & Kaplan 1972; Poutanen & Morris 1983). Marine humates are formed by condensation of carbohydrates, amino acids, and other simple sugars accompanied by cyclization to hydroaromatic and hydroxyaromatic acids (Nissenbaum & Kaplan 1972). Accordingly, the Rp value of 0.52 at 6–8 cm depth may suggest a high concentration of humic acids in the deeper parts of the Fællesstrand sediment. The Rp-C:N relationship seems to provide valuable informations on biological and chemical induced structural changes of organic matter occurring with depth in sediments.

Conclusions

The Rp index obtained from stepwise thermogravimetric analysis of organic matter appears to be widely applicable in ecological and biogeochemical studies. Generally, low Rp values (0.2–0.3) appear to represent aliphatic

carbohydrates and lipids, whereas high Rp values (0.5–0.7) is characteristic for proteins and polyphenolic compounds (humates). Together with elemental carbon and nitrogen analysis the Rp index provide a powerful two-dimensional tool for characterization of organic matter. The Rp-C:N relationship for living biogenic material follow a general negative logarithmic pattern, showing high Rp and low C:N for animal tissues rich in proteins, and low Rp and high C:N for plant materials rich in structural carbohydrates. The use of Rp in studies of detritus dynamics is complicated by the fact that proteins and humic compounds exhibit almost similar thermal combustion patterns. However, the Rp-C:N relationship can differentiate between those two groups of compounds, since C:N of proteins are 3–5 and that of humic compounds are 15–25. Thus, during early decomposition of organic material protein synthesis generally is responsible for a decrease in C:N and increase in Rp, whereas they both increase during the humification process of older detritus. The Rp-C:N relationship, however, will be even more valuable in organic matter characterization if it is combined with separate protein or humic analysis.

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