Elucidation of different forms of organic carbon in marine sediments of the Atlantic Coast of Spain by thermal analysis coupled to isotope ratio and quadrupole mass spectrometry

Elisa Lopez Capel[1], José Maria de la Rosa Arranz[2], Francisco J. González-Vila[2], José Antonio González-Perez[2], and David A.C. Manning[1]

1) School of Civil Engineering and Geosciences, University of Newcastle, Newcastle upon Tyne, NE1 7RU, UK. 2) IRNAS, C.S.I.C, Avda. Reina Mercedes, 10, P.O. Box 1052, 41080-Sevilla, Spain.

*corresponding author:Tel: +44 1912225964; Fax +44 101 2225322. E-mail: elisa.lopez-capel@ncl.ac.uk Present address: School of Civil Engineering and Geosciences, University of Newcastle, Newcastle upon Tyne, NE1 7RU, UK

Key words

Refractory organic matter, marine sediment, humic acid, TG-DSC, IRMS, QMS

Abbreviations

TG= Thermogravimetry

DSC= differential scanning calorimetry

IRMS= isotope ratio mass spectrometry

QMS= quadrupole mass spectrometry

m/z= ratio mass/charge,

Exotot= total TG weight loss for the temperature interval 200 – 600°C

Abstract

Analysis of river, estuary and marine sediments of the Atlantic coast of Spain by thermogravimetry-differential scanning calorimetry-quadrupole mass spectrometry-isotope ratio mass spectrometry (TG-DSC-QMS-IRMS) was used (a) to distinguish bulk chemical hosts for C within a sediment and humic acid fraction, (b) to track C pools with differing natural C isotope ratios, and (c) to observe variation with distance from the coast. This is the first application of such a novel method to the characterisation of organic matter from marine sediments and their corresponding humic acid (HA) fractions.

Using thermal analysis, a labile, a recalcitrant and a refractory carbon pool can be distinguished in the sediments. Extracted humic acids fractions are mainly of recalcitrant nature. The proportion of refractory carbon is highest in marine sediments and humic acid fractions.

Quadrupole mass spectrometry confirmed that the greatest proportion of *m/z* 44 (CO_2) and *m/z* 18 (H_2O) were detected at temperatures associated with recalcitrant carbon (510-540 ˚C).

IRMS analysis detected progressive enrichment in $\delta^{13}C$ of the sediment samples with an increase in marine influence. Isotopic heterogeneity of the refractory organic matter in marine sediments could be due to anthropogenic origin or natural combustion products. Isotope homogeneity of humic acids confirms the presence of terrigenous C within marine sediments, allowing terrestrial input to be characterised.

1. Introduction

The principal transport pathways that supply material derived from the continental crust to the oceans are river run-off and atmospheric deposition (Chester, 1990). Fluxes of carbon linking land and sea include those of dissolved and particulate organic matter (POM) (Alongi, 1998). POM is deposited in sediments, which rapidly accumulate in continental shelves. Due to its reduced reactivity and bioavailability organic matter reveals a high preservation potential in marine sediments (Holtvoeth et al, 2005). Severe recycling mechanisms occur in the sea (Smith and Mackenzie, 1987). Whatever processes are involved, they must allow extensive remineralization of intrinsically resistant terrigenous organic matter and subsequent preservation of seemingly more labile marine derived counterparts in marine sediments (Mayer et al, 1998). Thus, to understand global cycles of carbon and oxygen it is important to identify the mechanisms by which OM is preserved in near-shore marine sediments.

Soil organic matter (SOM) decomposition can be represented by three carbon pools. These include a labile (which includes cellulose (Lopez-Capel *et al*, 2005a), a recalcitrant (including lignin (Leinweber et al., 1992)), and a refractory pool (including chars (Kaloustian et al., 2001) as well as aromatic carbon (Lopez-Capel *et al*, 2006)). Decomposition models (such as ROTH-C) identify them respectively as 'microbial biomass', 'humified organic matter', and 'inert'. Various thermal analysis techniques have been used to characterise SOM (Turner and Schnitzer, 1962, Leinweber et al, 1992), to estimate their thermal stability (Dell' Abate et al., 2003), and to relate their thermal properties to biological decomposability (Lopez-Capel et al, 2005a; Plante et al., 2005). While the labile C pool is reactive (Sohi et al 2001) and susceptible to degradation (Lopez-Capel *et al*,2006), the recalcitrant C pool has a

low degradation rate, and the refractory C may remain in soil and sediments from centuries to millennia (Gonzalez-Perez et al 2004).

The determination of refractory forms of organic matter in sediments is relevant in order to improve current estimates of carbon fluxes from the biosphere to the sedimentary C pool. Refractory forms of organic matter, such as humic-like materials and black carbon, can represent a significant sink for carbon dioxide due to the transfer of carbon from the relatively fast biological-atmosphere carbon cycle to the long-term geological carbon cycle (Middelburg et al., 1999; Gustafsson et al., 2001). Due to their important geochemical and environmental implications, there is an increased interest in the study of the different forms of refractory organic matter (ROM) widely dispersed in soils, water and sediments.

The labile SOM fraction decomposes during thermal analysis at approx. 300-350 °C, while the more recalcitrant SOM decomposes at approximately 400-500 °C (Lopez-Capel $et\ al$, 2005$_{a,b,}$). Refractory organic matter has been reported to decompose at 430-530 °C, and is composed of either artificial chars (Kaloustian et al., 2001) or natural aromatic compounds (Lopez-Capel $et\ al$, 2006). Inorganic carbon, such as carbonates, can also be determined from decomposition between 700-900 ˚C.

Extending the capability of thermal analysis, the coupling of an isotope ratio mass spectrometer (IRMS) and a quadrupole mass spectrometer (QMS) to a thermal analysis system (TG-DSC) allows the proportions of the major components, evolved gas composition and carbon isotope ratios of composite organic/inorganic materials to be determined during a single heating experiment. The distinction of isotope signatures of labile, recalcitrant, and refractory components proves new insights into the dynamics of organic matter in sediments.

The area of study is of environmental interest due to deposition of river derived sediments over a surface of 90.000 Km^2. Deep Mediterranean currents affect sediment accumulation, and are partly responsible for the mobilisation, transport and deposition of large amounts of detritus on the continental shelf and slope, favouring turbidite formation (Bonnin *et al*., 1975, Martínez de Olmo *et al*., 1984, Flinch *et al*., 1996, Somoza *et al*., 1994, Berasategui *et al.*, 1998, Battista *et al*., 2000). Middleburg et at (1999) previously quantified refractory organic matter (ROM) in marine sediments (between 175 and 4909 m deep) near the area of study, detecting between 16 and 29% total organic carbon (TOC).

Sedimentary organic matter is characterised by organic geochemical methods, such as elemental analysis, stable carbon isotope analysis, Rock-Eval Pyrolysis, and lignin chemistry (Holtvoeth et al, 2005). This is the first application of thermal analysis coupled to quadrupole and isotope ratio mass spectrometry to the characterisation of organic matter from marine sediments in the Atlantic coast of Spain.

The aim of this work was to determine carbon fluxes from the continent to the ocean using thermal analysis coupled to isotope ratio mass spectrometry (IRMS) to discriminate organic fractions of differing biological origins that cannot be distinguished using bulk analysis methods.

2. Materials and methods

2.1 Materials

During the 2000 and 2001 BACH Project cruise (BC, REN 2002-04602-C02), surface sediment samples (20cm depth) were taken from the internal continental platform and from the Guadiana estuary coast, as part of the project "Environmental geochemistry of sediments from the Huelva coast". The sampling area is shown in Figure 1. Over 200 samples, representing the estuary area, were taken. These samples were thought to have high OM content, and be susceptible to high amounts of refractoty organic matter (ROM), such as black carbon.

To minimize variation, each sample was a composite sample made from 5 subsamples taken in the sampling plot. All the samples were stored frozen in glass containers to avoid microbial growh. Before analysis samples were freeze dried, thoroughly ground in a mortar mill and homogenised to reduce variability between replicates. For the study of ROM, humic acid (HA), humin (HU), refractory organic matter (ROM) were extracted and isolated from marine sediments.

Humic substances were alkaline extracted with aqueous NaOH, followed by precipitation of humic acid at low pH (McCarthy and Malcolm, 1979). Standard humic acid/fulvic acid (HA/FA) separation includes an acid treatment producing carbonate-free humic and fulvic acids. The insoluble fraction was further demineralised. In detail, the following treatments were successively applied to all the samples: i) lipid extraction at 40-60ºC with a solution of dichloromethane/methanol (3:1), for 16h, ii) removal of extractable humic fractions (HA/FA) by successive extractions with 0.1M $Na_4P_2O_7$ and 0.1M NaOH; this procedure was repeated five times, and the dark brown supernatant solution (total humic extract) was then

separated from the insoluble fraction (humin) by centrifugation at 15000rpm for 15 minutes; iii) demineralization of the humin fraction in a solution of 6M HCl and a 6M 1:1 HCl/HF solution (Lim & Cachier., 1996).

A set of subsamples, representing the area of study, were selected on the basis of total organic matter (OM) content, and the distance to the coast. They consist of 1 river (R25), 3 estuary (E209, E220, and E226) and 2 marine (M131, M155) samples. Bulk sediments (R25S, E209S, E220S, E226S, M131S, and M155S) and humic acids (R25HA, E209HA, E220HA, E226HA, M131HA, and M155HA) were analyzed by TG-DSC-QMS-IRMS. Preliminary thermal analysis of the humin fractions showed the presence of quartz, with only 5-10% weight loss. Because of their low reactivity (i.e. very low humin content), the humin fraction was not studied further.

2.2 Analysis

TG-DSC-QMS-IRMS evolved gas analysis was carried out by simultaneously coupling the TG-DSC system through an adapter head in the STA 449C Jupiter gas outlet (a) via a 200 °C heated capilliary to a Netzsch Aeolos QMS 403C quadrupole mass spectrometry system (*m/z* range 10 – 300) and (b) by a separate capilliary via a PDZ ANCA S/L interface module to a PDZ Europa 20:20 isotope ratio mass spectrometry system (Lopez-Capel et al 2005b, 2006).

Approximately 30 mg of sediment or 10mg of HA were placed in an alumina crucible. Samples were heated at a heating rate of 20 °C min^{-1}, from ambient temperature to 650 °C under flowing 20% oxygen in helium (50 cm^3 min^{-1}) and from 650 to 1000 °C under helium only (for carbonate analysis).

For QMS analysis the evolved gas was sampled and analyzed by the mass spectrometer throughout the course of the desorption process. Mass/charge (m/z)

values from 10 to 300 were collected and *m/z* intensities of interest (12 (C), 18 (H_2O), 26 (CN), 27 (HCN), 30 (NO), 44 (CO_2 & N_2O), 45 ($^{13}C^{16}O_2$) and 46 (NO_2), were reported. These masses have previously been detected in evolved gases derived during thermal analysis from humic substance (Dell' Abate et al. 2003) and coal samples (Varey et al., 1996). The number of *m/z* signals selected gave a temporal resolution of 10s corresponding to a temperature change of approximately 2°C. The signals were exported to the NETZSCH software for analysis versus temperature. In order to compare the relative intensity of m/z peaks for different samples the signals from the QMS were normalised to the total intensity (Arenillas et al., 1999).

For IRMS analysis, six gas samples were taken during the TG-DSC heating profile between 290 and 900 ºC for sediments, and between 290 and 600 ºC for HA. These gas samples correspond to the gas evolved at 350, 510, 540, 620, 700, and 740 ºC for sediments, and 350, 430, 510, 540, 596, and 620 ºC for HA. These temperatures correspond to reactions detected by DSC. Reference CO_2 gas ($\delta^{13}C=$ -29.88 ‰) was sampled 3 times at the beginning and 3 times at the end of each run.

Bulk carbon isotope values were obtained by off-line measurements using an ANCA S/L Prep unit attached to a PDZ Europa 20/20 isotope ratio mass spectrometer. Carbon isotope values were expressed in per mil (‰) notation relative to the Pee Dee Belemnite (PDB) standard.

Total carbon percentage (TC), total organic carbon (TOC), and total nitrogen (TN) of bulk sediments and humic acids were determined by Carbo-Elba Elemental Analyser.

To examine sediment mineralogy, samples were analysed by X-ray diffraction using a Phillips – binary XRD with an Xpert MPD diffractometer, scanning from 7-70 °2θ.

3. Results and discussion

3.1 Thermal analysis (TG-DSC)

Thermogravimetric (TG) mass losses were observed at various temperature ranges, as shown by the more negative slopes in the TG thermograms. These mass losses can be associated with the decomposition of different carbon groups based on previous literature (Lopez-Capel et al 2005a; Manning et al., 2005; Plante et al 2005; Dell' Abate et al 2003) as follows: labile C (200-400 ºC), recalcitrant C (400-550 ºC), refractory C (550-650 ºC), and carbonates (650-900 ºC) (Figure 2a).

TG parameters of the sediments and humic acid samples studied are summarized in Table 1, and bulk composition parameters are given in Table 2. From the observed weight losses the relative proportions of labile, recalcitrant and refractory carbon can be estimated. Using Dell' Abate and colleagues (2000) terminology in Table 1, stability indices (Exo 1, Exo 2, and Exo 3) are calculated from the relative percentage of the weight loss corresponding to the first exotherm (aliphatic C and carbohydrates –predominantly cellulose), second exotherm (aromatic C, predominantly lignin and recalcitrant C), and third exotherm (poly-condensed forms of lipids and aromatic C) normalized with respect to the total weight loss between 200 and 650 °C (Exotot).

Table 1 shows that the percentage of labile C (Exo1) in sediments decreases, while the percentage of refractory C (Exo3) increases from river to marine samples. The greatest weight loss (46 % of the total weight loss associated with organic matter, called Exotot), is associated with the recalcitrant C (Exo2). Carbonate content was greatest in the two marine sediment samples (M131S and M155S).

There was little variation between weight losses in river, estuary and marine (Exo1, 2, and 3) in humic acid fractions. The major weight loss was again associated with recalcitrant organic matter (Exo 2).

The highest amount of refractory carbon was present in the marine samples (M131S, M131HA, M155S and M155HA). Artificial char, from the combustion of labile materials during the thermal analysis process, could contribute to Exo 3, as previously described in the literature (Kaloustian et al, 2001, Varey et at 1996, Lopez Capel et al, 2006). Soot, originated from fossil fuel and biomass burning, has been found to dominate black carbon input in open shelf sediments (Gustafsson and Gschwend, 1998). BC has been detected in extracted humic acids before, although concentrations were generally low (2 to 22%) (Sympson and Hatcher, 2004). It is possible that the high thermal stability of humic acids, such as M131HA and M155HA, could be derived from black carbon (charred plant materials, soot) and not from native plant materials (Haumier and Zech, 1995).

DSC traces of sediments and humic acids (Figure 2 b and c, respectively) showed changes in the contributions of labile C (300-350 ºC), recalcitrant C (480-520 ºC) and refractory C, (560-590 ºC) C within the samples (riverine, estuarine and marine). The sediment samples have two exothermic peaks at 340 ºC and 510-526 ºC. The two marine sediments also have an endothermic peak at 690 ºC. Most humic acids showed a main exothermic peak at 490-520 ºC followed by a shoulder at 520-594 ºC.

The first DSC exothermic peak in the sediment samples is attributed to decomposition of labile materials, such as cellulose (Kaloustian et al., 2001). Peaks at 300-350°C have previously been observed in soils (Satoh 1984, Dell' Abatte et al 2002, Lopez Capel et al 2005a). This first DSC peak was not present in the humic

acid samples. This could be due to the extraction procedure. Lipids were extracted prior to HA extraction, and these may account for a high percentage of the labile material. The lipid content decreased in the same order as Exo1: river<estuary<marine (see Table 2). R25HA is the only sample showing a peak at 417 °C, which for solid samples is attributed to lignin (Lopez Capel et al 2006). A shoulder peak at around 400-450 °C is possibly attributed to recalcitrant materials in the sediments. However, this reaction could have been affected by mineral dilution and was unclear. The second peak at 450-550 °C, in sediments and humic acids, is attributed to combustion of the recalcitrant OM and/or char materials (Lopez-Capel et al., 2005a,b, 2006). A third exothermic peak was detected for humic acids at 550-650 °C, which could be attributed to refractory forms of organic matter. This third peak may reflect decomposition of materials such as black carbon (BC) and/or kerogen, however, further pyrolytic analysis of this fraction would be needed to confirm this possibility. Exothermic peaks between 507 and 570 °C have previously been observed in humic acid extracted from soils (Dell' Abatte et al 2002), and coal (Varey et al 1996). Marine sediments (M131S and M155S) had a further endothermic peak at 690 °C, which could be attributed to calcium carbonate.

Percentages of carbon and nitrogen composition parameters of sediments and humic acids are summarized in Table 2. There is little variation in total organic carbon (TOC %) and total nitrogen (TN %) in both sediment and humic acid fractions. Thermal analysis was able to differentiate carbon groups in these samples. Exothermic ratios Exo1/Exo2 have previously been related to C/N ratios (Dell' Abatte et al 2003; Lopez Capel et al 2006). The sediment recalcitrant fraction (Exo 2) negatively correlates with C/N ratio (r^2=0.7518), TOC (r^2=0.6103) and the lipid

content (r^2=0.7042). There was no correlation between the humic acid fractions and other parameters reported in Table 2.

C/N ratios from bulk organic matter have been used in many studies to distinguish between phytoplankton and land-plant sources, with the former typically yielding low values (4–10) and the latter tending to have ratios >20 (Meyers, 1994; Meyers, 1997).

Marine systems close to land, and lakes, generally show intermediate C/N values, reflecting mixing of terrestrial and aquatic organic matter (Prahl et al., 1994; Silliman et al., 1996). Increasing or decreasing ratios have therefore been used to infer relative change in organic matter sources for both marine (Calvert et al., 2001; Jasper and Gagosian, 1993) and lacustrine (Kaushal and Binford, 1999; Talbot and Johannessen, 1992) sediments, even though these ratios can increase somewhat upon degradation (Thornton and McManus, 1994).

The range of C/N ratios for all samples includes values that characterise both aquatic phytoplankton and land plants, but with most samples suggesting that the organic matter represents a mixture of marine and terrestrial carbon. Consequently, proximity to sources of land plant debris, and marine organic productivity should be important controls. This would imply that samples R25S and E226S have higher terrigenous contribution, while samples E209S, E220S, M131S, and M155S have a higher contribution of marine carbon.

3.2 XRD Analysis of sediments

River and estuary particulate material (RPM and EPM) contain aluminosilicate minerals (such as clays), quartz, and carbonates. The presence of clay minerals and carbonates may affect the TG-DSC trace of organic matter in sediments

but not of the isolated humic acid fractions. XRD analysis was used to examine the clay mineralogy of the sediment samples. Diffractograms resulting from XRD analysis of sediments were compared to those of reference materials and indicated the presence of kaolinite, illite-muscovite, quartz and calcite in all sediment samples. Dolomite was also detected in riverine and marine sediments and the feldspar albite in estuarine sediments. Although clay minerals were detected in marine sediments, amounts were low, and diffractograms were dominated by quartz and calcite. In order to assess the contribution of the thermal decomposition of clay minerals to the exothermic peaks in the temperature ranges 300-650 ºC, reference samples of clay minerals known to be present in sediments (determined by XRD) were analysed by TG-DSC under the same analytical conditions as the sediments. Illite releases interlayer water at 440-460 ºC and kaolinite at 510-530 ºC in endothermic reactions. Quartz undergoes a phase transition at 573 ºC as an endothermic reaction with no associated weight loss. TG-DSC analysis of calcite releases CO_2 at 680-700 ºC in an endothermic reaction.

3.3 QMS analysis

Sediments and humic acids were analyzed by QMS to assess the evolution of gas species which may relate to C dynamics in the sediment's OM fraction. The only degradation fragment masses that were detected consistently for all samples were CO_2 (*m/z* 44) and H_2O (*m/z* 18). Volatiles were released at the lowest temperatures (~350 ºC), followed by decomposition of recalcitrant OM (450 ºC), and refractory OM (500 ºC). Similar findings have previously been reported in soils (Dell'Abatte et al 2003, Lopez Capel et al 2005b) and compost (Lopez Capel et al 2006).

The relative ion intensities of gas species CO_2 (m/z 44) and H_2O (m/z 18) observed during thermal analysis of sediments and humic acids are presented in Figure 3. QMS analysis showed that the maximum amount of gas (CO_2) evolved from the combustion of sediments and humic acids was at 510-540 °C followed by a shoulder peak at 600-620 °C. The exceptions were the river sediment, with maximum amount of gas (CO_2) at 350 °C, and the marine sediments (131 and 155) with the highest evolution of CO_2 at 700-720 °C.

The maximum amounts of water (m/z 18) evolved from the combustion of sediments and humic acids were at 510-540 °C, and at 350 °C for the river sediment samples (Figure 3). Traces of H_2O were detected at 100-120 °C, 300-350 °C, 510-540 °C, 600-620 °C for all samples and also at 700-720 °C for marine sediments (131 and 155).

Gas evolution peaks at the temperature ranges mentioned are associated with the release of free water at 120 °C, with reactions of labile C at 350 °C , recalcitrant C at 510 °C, refractory C at 620 °C, and carbonate decomposition at 700 °C. There would also be release of water in sediments at 440 and 520 °C from the decomposition of clay minerals, such as illite and kaolinite, respectively. These may further release organic matter physically trapped in clay particles (Plante et al 2005).

3.4 IRMS Analysis

There is progressive ^{13}C enrichment of the sediment samples with an increase in marine influence (Figure 4). Table 3 summarises the $\delta^{13}C$ values of sediments and humic acids at various temperature ranges during thermal degradation. In general, bulk $\delta^{13}C$ values are approximately 4 ‰ more negative than those determined for organic matter using TG-DSC-IRMS (Lopez-Capel et al, 2005b).

The isotope ratio for C3 biomass ranges from -23 to -34 ‰, with an average of about -27 ‰ (Meyers, 1997), while typical marine end-member values are -18 to -20 ‰ for $\delta^{13}C_{org}$ (Holtvoeth et al, 2005). Taking into account the systematic 4 ‰ difference between the TAIRMS methodology and bulk analysis, the river sediments have terrestrial signal, marine sediments have a marine signal, estuary sediments are a mixture of both. All humic acid fractions have a terrestrial signal, irrespective of the sample type. It is possible that the TG-DSC-IRMS data for whole samples include a contribution from anthropogenic black carbon or natural combustion products, for which $\delta^{13}C$ values are reported to range from -22.5 to -26.5 ‰ (Glaser et al, 2005).

There is great isotopic variability between the sediments (mean TAIRMS - 12.8 ‰ ± 4.5) but little variability between the humic acids (mean TAIRMS 20.1 ‰ ± 1.75). Bulk ANCA isotopic values agree with this observation, with mean sediment values of -17.1 ‰ ± 6.9 and mean humic acid values of -24.7‰ ± 1.13. Notice that the bulk values of marine sediments were affected by carbonate content, and that there is -4.41 ‰ difference between the ANCA bulk analysis and TAIRMS values. Such difference between the methodologies has previously been observed (Lopez-Capel et al., 2005b, 2006).

Sediments at 350 °C show $\delta^{13}C$ enrichment with an increase in marine influence, which could be partitioned into that due to local high plant inputs, and that due to mineral, algal and non-local macrophyte inputs (Middelburg et al, 1997). Values in marine sediments (M131S, M155S) at 350 °C could be attributed to algae (-17 ‰) and plankton derived material (eg. Middelburg et al, 1997). Sediments show $\delta^{13}C$ enrichment with an increase in decomposition temperature (from 350 to 620 °C) in river and estuarine sediments.

The greatest $\delta^{13}C$ difference between the samples was at 540 °C, by 14.0 ‰ between river and marine. This temperature corresponds with the maximum amount of CO_2 evolved from the combustion of sediments. The river samples $\delta^{13}C$ values range between-17.2 and -17.7 ‰, estuary between -16.5 and -13.6 ‰, and marine samples between -8.2 and -3.0. The isotopic enrichment in marine sediments (M131S and M155S) is higher than values reported for marine vegetation. It is possible that isotopic variability in the marine samples could be due to microbial methanogenesis of refractory organic matter, probably kerogen. Clayton (1991) describes differing C isotopic fractionation for the formation of methane from labile and refractory kerogen. When methane formation occurs during the oxidation of organic matter, two metabolic pathways operate. The process involved is kinetically controlled, enriching ^{13}C in the residual CH_4, and ^{12}C in the respired CO_2 (the opposite effect to CH_4 generation). The fractionation involved ranges from 1.002 to 1.014, with $\delta^{13}C$ CO_2 values ranging from -33 to +18 (Whiticar & Faber, 1986). This may account for the observed enrichments in ^{13}C. Additionally, carbonate-derived contributions were detected at 700-720 °C in marine samples (-2.0‰ for M131S and -6.2‰ for M155S), with C isotopic values in the range associated with marine carbonates (Gawenda et al 1999).

Values for $\delta^{13}C$ for the humic acids show little variation for samples analysed using TG-DSC-IRMS (Figure 5), with a mean of -20.7 ± 1.75. This is consistent with a homogeneous input of terrestrial origin. The humic acids from the marine sediment samples are slightly more enriched in $\delta^{13}C$, bearing in mind that values for gas samples at 350 °C are less reliable as gas yields were very low at this temperature.

4. Conclusion

In the Huelva coast region, systematic changes have been observed in the proportions and bulk characterisation of sedimentary organic matter. Terrestrial influences, in terms of proportions of labile organic matter and $\delta^{13}C$ values, decrease towards the ocean. In contrast, chemically extracted humic acids show very consistent compositions in terms of thermal behaviour through the system, and have constant $\delta^{13}C$ values.

We conclude that terrestrial humic acids, derived from soils, retain carbon isotopic composition irrespective of their location in the system. The relative contributions of soil organic matter vary according to the amount of marine input, which includes carbonate minerals in fully marine systems.

This study demonstrates that humic acids can be recognised as a homogeneous C pool within marine sediments, allowing the terrestrial input to be characterised.

References

Alongi, D.M., 1998. Coastal Ecosystem Processes, CRC Press. Boca Raton, Florida

Arenillas, A., Rubiera, F., Pis, J.J., 1999. Journal of Analytical and Applied Pyrolysis. 50, 3138.

Battista, B..M., Lowrie, A., Makarov, V., Moffett, S.J., Somoza, L., 2000. Lateral tectonics in the Gulf of Mexico, Gulf of Cadiz, and the Middle America Trench: Impacts on hydrocarbon accumulations. In: Deep-water Structure and Stratigraphy as a Paired Process/Response System, Expanded Abstracts. American Association of petroleum Geologists and Society of Economic Paleontologists and Mineralogists (AAPG), Tulsa.

Berástegui, X., Banks, C.J., Puig, C., Taberner, C., Waltham, D., Fernández, M., 1998. Lateral diapiric emplacement of Triassic evaporates at the southern margin of the Guadalquivir Basin, Spain. In: Mascle, A., Puigdefabregas, C., Luterbacher, H.P. and Fernández, M., (Eds.), Cenozoic Foreland Basins of Western Europe. Geological Society Special Publications 134, pp. 4968.

Bonnin, J., Olivet, J.L., Auzende, J.M., 1975. Structure en nappe a l'ouest de Gibraltar. C.R. Academy of Science 280, 559562.

Calvert, S.E., Pedersen, T.F. Karlin, R.E., 2001. Geochemical and isotopic evidence for post-glacial palaeoeceanographic changes in Saanich, Inlet, British Columbia. Marine Geology 174, 287–305.

Clayton, C., 1991. Carbon isotope fractionation during natural gas generation from kerogen. Marine and Petroleum Geology, 8, 232240.

Dell´Abate, M.T.,Canali, S., Trinchera, A., Benedetti, A., Sequi, P., 2000. Thermal methods of organic matter maturation monitoring during a composting process. Journal of Thermal Analysis and Calorimetry 61, 389396.

Dell'Abate, M.T., Benedetti, A., Trinchera, A., Dazzi., C., 2002. Humic substances along the profile of two Typic Haploxerert. Geoderma, 107, 281–296.

Dell'Abate, M.T., Benedetti, A., Brookes, P.C., 2003. Hyphenated techniques of thermal analysis for characterisation of soil humic substances. Journal of Separation Science 26, 433440.

Flinch, J., Bally, A., Wu, S., 1996. Emplacement of a passive-margin evaporitic allochthon in the Betic Cordillera of Spain. Geology 24, 6770.

Gawenda, P., Winkler, W., Schmitz, B., Adatte, T., 1999. Climate and bioproductivity control on carbonate turbidite sedimentation (Paleocene to earliest Eocene, Gulf of Biscay, Zumaia, Spain. Journal of Sedimentary Research 69,1253-1261.

Glaser, B., Dreyer, A., Bock, M, Fiedler, S., Mehring, M., Heitmann, T., 2005. Environmental Science & Technology 11, 39113917.

González-Pérez, J.A., González-Vila, F.J., Gonzalo Almendros G., and Knicker, H., 2004. The effect of fire on soil organic matter—a review. Environment International 30, 855870.

Gustafsson, Ö., Gschwend, P.M., 1998. The flux of black carbon to surface sediments on the New England continental shelf, Geochimica et Cosmochimica Acta 62, 465–472.

Gustafsson, O., Bucheli, T.D., Kukulska, S., Anderson, M., Largeau, C., Rouzaud, J.N., Reddy, J.M., Eglinton T.I., 2001. Evaluation of a protocol for the quantification of black carbon in sediments. Global Biochemistry 15, 881890.

Haumaier, L., Zech, W., 1995. Black carbon- Possible sources of highly aromatic components of soil humic acids. Organic Geochemistry 23, 191196.

Holtvoeth, J., Kolonic, S., and Wagner, T., 2005. Soil organic matter as an important contributor to late Quaternary sediments of the tropical West African continental margin. Geochimica et Cosmochimica Acta 69, 20312041.

Jasper, J.P., Gagosian, R.B., 1993. The sources and deposition of organic matter in the Late Quaternary Pygmy Basin, Gulf of Mexico. Geochimica et Cosmochimica Acta 54, 117–132.

Kaloustian, J., Pauli, A.M., Pastor, J., 2001. Kinetic study of the thermal decompositions of biopolymers extracted from various plants. Journal of Thermal Analysis and Calorimetry 63, 7–20.

Kaushal, S., Binford, M.W., 1999. Relationship between C:N ratios of lake sediments, organic matter sources, and historical deforestation in Lake pleasant, Massachusetts, USA. Journal of Paleolimnology 22, 439–442.

Leinweber, P., Schulter, H.R., Horte, C., 1992. Differential thermal analysis, thermogravimetry and pyrolysis-field ionisation mass spectrometry of soil organic matter in particle-size fractions and bulk soil samples. Thermochimica Acta 194, 175−187.

Lim, B., Cachier, H., 1996. Determination of black carbon by chemical oxidation and thermal treatment in recent marine and lake sediments and Cretaceous–Tertiary clays. Chemical Geology 131, 143154.

Lopez-Capel, E., Sohi, S.,, Gaunt, J.L., Manning, D.A.C., 2005a. Use of Thermogravimetry-Differential Scanning Calorimetry to characterize modelable soil organic matter fractions. American Journal of Soil Science. Society. 69, 136140.

Lopez-Capel, E., Bol, R, Manning, D.A.C., 2005b. Application of simultaneous thermal analysis mass spectrometry and stable carbon isotope analysis in a

carbon sequestration study. Rapid Communications in Mass Spectrometry 19, 31923198.

Lopez-Capel, E., Abbott, G.D., Thomas K.M., Manning D.A.C., 2006. Coupling of thermal analysis with quadrupole mass spectrometry and isotope ratio mass spectrometry for simultaneous determination of evolved gases and their carbon isotopic composition. Journal of Analytical and Applied Pyrolysis 75, 8289.

Manning, D.A.C., Lopez-Capel, E, Barker, S., 2005. Seeing soil carbon: use of thermal analysis in the characterization of soil C reservoirs of differing stability. Mineralogical Magazine 69 , 425435.

Martínez de Olmo, W., García-Mallo, J., Leret, G., Serrano, A., Suárez, J., 1984. Modelo tectosedimentario del Bajo Guadalquivir. Proceedings on the II Spanish Geological meeting 1, pp. 199213.

Mayer, L.M., Keil, R.G., Macko, S.A., Joye, S.B., Ruttenberg, K.C., Aller, R.C., 1998. Importance of suspended particulates in riverine delivery of bioavailable nitrogen to coastal zones. Global Biogeochemical Cycles 12, 573579.

McCarthy, P., Malcolm, R.L., 1979. The need to establish a reference collection of humic substances. In: Chesier, S.N., Hertz, H.S. (Eds), Trace Organic Analysis: A New Frontier in Analytical Chemistry. U.S. National Bureau of Standards 519793.

Meyers, P.A., 1994. Preservation of elemental and isotopic source identification of sedimentary organic matter. Chemical Geology 114, 289–302.

Meyers, P.A., 1997. Organic geochemical proxies of palaeooceanographic, palaeolimnological, and palaeoclimatic processes. Organic Geochemistry 27, 213–250.

Middelburg, J. J., Nieuwenhuize, J., Lubberts, R. K., Van de Plassche, O., 1997. Organic Carbon Isotope Systematics of Coastal Marshes. : Estuarine, Coastal and Shelf Science 45, 681–687.

Middelburg, J.J., Nieuwenhuize, J., Breugel, P., 1999. Black carbon in marine sediments. Marine Chemistry 65, 245252.

Plante, A.F., Pernes, M., Chenu, C., 2005. Changes in clay-associated organic matter quality in a C depletion sequence as measured by differential thermal analyses. Geoderma, 129, 186199.

Prahl, F.G., Ertel, J.R., Goni, M.A., Sparrow, M.A., Eversmeyer, B., 1994. Terrestrial organic carbon contributions to sediments in the Washington margin. Geochimica et Cosmochimica Acta 58, 3048–3055.

Satoh, T., 1984. Thermal nature of organo-mineral complex particles and their humic substances. Soil Science and Plant Nutrition 30, 95104.

Silliman, H.E., Meyers, P.A., Bourbonniere, R.A., 1996. Record of postglacial organic matter delivery and burial in sediments of Lake Ontario. Organic Geochemistry 24, 463472.

Smith, S.V., Mackenzie, F.T., 1987. The ocean as a net heterotrophic system: Implictions for the carbon biogeochemical cycle. Global Biogeochemical Cycles 1, 187198.

Sohi, S. P., Mahieu, N., Arah, J.R.M., Powlson, D.S., Madari, B., Gaunt, J.L., 2001. A procedure for isolating soil organic matter fractions suitable for modeling. Soil Science Society of America Journal, 65, 1121–1128.

Somoza, L., de Andres, J.R., Rey, J., Hernandez-Molina, J., Rodriguez-Vidal, J., Clemente, L., Rodriguez-Ramirez, A., Diaz-del-Rio, V., 1994. Morpho-depositional evolution of the Cadiz Gulf continental shelf: Golca project.

Proceedings del 1º Simpósio Sobre A Margen Continental Ibérica Atlántica, Lisboa, Portugal.

Sympson, M.J., Hatcher, P.G., 2004. Determination of black carbon in natural organic matter by chemical oxidation and solid-state ^{13}C nuclear magnetic resonance spectroscopy. Organic Geochemistry 35, 923935.

Talbot, M.R., Johannessen, T., 1992. A high resolution palaeoclimatic record for the last 27,500 years in tropical West Africa from the carbon and nitrogen isotopic composition of lacustrine organic matter. Earth and Planetary Science Letters 110, 23–37.

Thornton, S.F., McManus, J., 1994. Application of organic carbon and nitrogen stable isotope and C/N ratios as sources indicators of organic matter provenance in estuarine systems: evidence from the Tay Estuary, Scotland. Estuarine, Coastal and Shelf Science 38, 219–233.

Turner, R.C., Schnitzer, M., 1962. Thermogravimetry of the organic matter of a Podzol. Soil Science 93, 225232.

Varey, A., Hindmarsh, C.J., Thomas, K.M., 1996. The detection of reactive intermediates in the combustion and pyrolysis of coals, chars and macerals. Fuel 75 , 164176.

Whiticar, M.J., Faber, E., Schoell, M., 1986. Biogenic methane formation in marine and fresh water environments: CO_2 reduction vs acetate fermentation isotope evidence. Geochimica et Cosmochimica Acta 5, 693709.

Table 1. Thermogravimetry (TG) and Differential scanning calorimetry (DSC) parameters of sediments and humic acids summarizing: total weight loss (% ± 1%) for the temperature interval 200 – 650 °C (Exotot), relative weight losses (%) of temperature intervals Exo1 (200-400 °C),Exo2 (400-550 °C),and Exo3 (550-650 °C), % CaCO3* and temperature (°C± 3 °C) of exothermic and endothermic peaks.

sediments	Exo 1	Exo 2	Exo 3	Exotot	%CaCO3*	1st DSC exotherm (°C)	2nd DSC exotherm(°C)	1st DSC endotherm (°C)
R 25S	44.29	43.19	12.52	7.23	1.84	342	496	
E 209S	29.72	47.24	23.03	5.96	1.23	356	524	
E 220 S	35.29	47.06	17.65	0.76	0.02	336	526	
E 226S	31.78	46.03	22.19	7.71	2.36	346	522	
M 131S	20.24	46.47	33.30	12.97	8.25	349	512	693
M 155S	19.25	47.45	33.30	13.25	7.77	347	515	690

humic acid	Exo 1	Exo 2	Exo 3	Exotot	1st DSC exotherm (°C)	2nd DSC exotherm (°C)	3rd DSC exotherm (°C)
R 25HA	35.23	58.80	5.97	82.53	417	503	584
E 209HA	30.41	59.32	10.27	78.82	none	505	527
E 220 HA	33.01	64.87	2.12	82.58	none	499	564 (s)
E 226HA	33.40	65.77	0.83	77.29	none	489	none
M 131HA	32.60	51.09	16.31	85.07	486	520	594
M 155HA	29.08	17.65	53.27	71.02	none	544 (s)	670

* % CaCO3 calculated from the equation: mass of calcite = weight loss (%) from the release of CO2 (650-850 °C) x 100/44 where CaCO3(100RMM) →CaO(56RMM) +CO2(44RMM)

Table 2. Percentages ($\pm$ 5%) of composition parameters of sediments and humic acids summarizing: total carbon (TC%), total nitrogen (TN%), total organic carbon (TOC %), total inorganic carbon (TIC %), organic carbon over total nitrogen ratio (C_{org}/N_{tot}), and percentages of extracted lipids, humic acids and humin enriched fractions from sediments.

Sediment	TC (%)	TN (%)	TOC (% C_{org})	TIC (% C_{in})	C_{org}/N_{tot}	Lipids (%)	Humic acids (%)	Humin (%)	Humic Acid	TC (%)	TN (%)
R25S	1.84	0.13	1.75	0.11	13.46	0.33	0.53	27.8	R25HA	49.50	4.30
E209S	1.69	0.16	0.77	0.92	4.81	0.16	0.46	51.9	E209HA	49.29	4.07
E220S	1.74	0.19	1.43	0.31	7.53	0.16	0.49	36.7	E220HA	47.31	4.52
E226S	1.19	0.10	1.16	0.03	11.60	0.12	0.58	44.6	E226HA	45.93	4.67
M131S	3.11	0.16	1.17	1.94	7.31	0.07	0.42	40.5	M131HA	49.12	4.66
M155S	3.11	0.15	1.09	2.02	7.27	0.07	0.40	41.7			

Table 3 $\delta^{13}C_{v\text{-PDB}}$ values of sediments and humic acid fractions at various temperatures during thermal degradation (± 0.04‰ determined by TG-DSC-IRMS), and bulk $\delta^{13}C_{v\text{-PDB}}$ values (± 0.05‰ determined by ANCA-IRMS), (n.d. = not determined).

sample	350 °C[#]	510 °C	540 °C	620 °C	700 °C	720 °C	bulk 13C
R25S	-19.7	-17.5	-17.2	-17.7	-21.0	-20.9	-23.8
E209S	-18.1	-14.7	-13.6	-11.2	-11.9	-13.5	-19.9
E220S	-20.9	-15.1	-13.8	-14.6	-23.4	-23.5	-22.7
E226S	-20.3	-16.5	-15.3	-10.9	-15.8	-16.5	
M131S	-17.1	-10.4	-8.17	-3.24	-2.02	-2.02	-9.77
M155S	-16.3	-6.13	-3.01	0.34	-6.20	-7.15	-9.75

sample	350 °C	430 °C	510 °C	540 °C	595 °C	620 °C	bulk 13C
R25HA	-18.7	-19.9	-20.5	-20.4	-20.7	-20.9	-24.9
E209HA	-19.9	-20.7	-22.1	-22.1	-21.9	-21.8	-25.4
E220HA	-20.4	-21.1	-22.6	-22.3	-22.1	-22.1	-25.3
E226HA	-18.5	-20.5	-21.7	-21.7	-21.8	-21.8	
M131HA	-16.2	-17.6	-19.3	-19.3	-19.4	-19.5	-23.0
M 155 HA	-12.8	-17.4	-19.8	-19.4	-17.7	-16.9	

Figure 1. Sampled area in the South West Iberian Peninsula with an indication of the sediments used in this study.
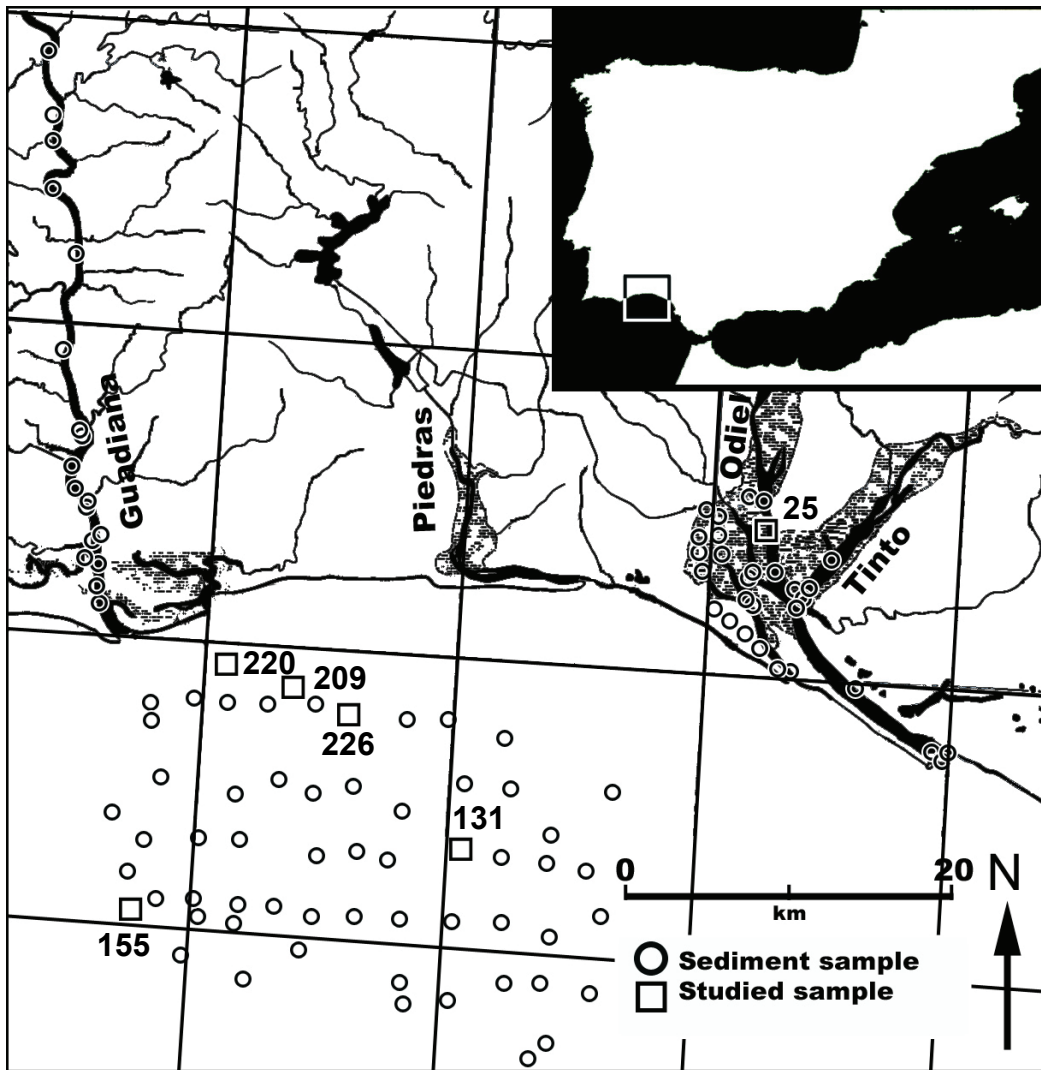
Figure 2 Thermogravimetric traces (TG) of sediments (a) and differential scanning calorimetric (DSC) traces of sediments (b) and humic acids (c)
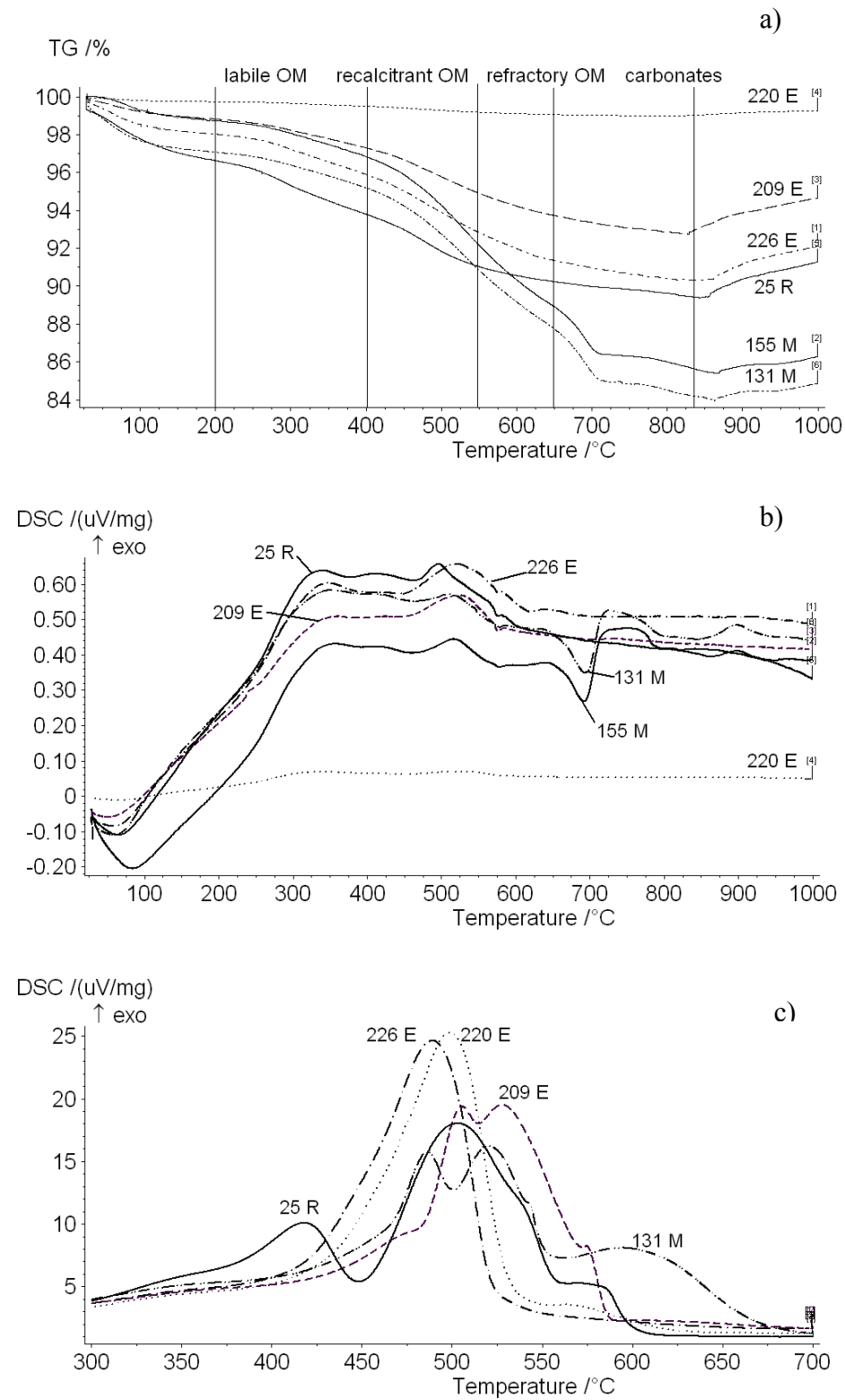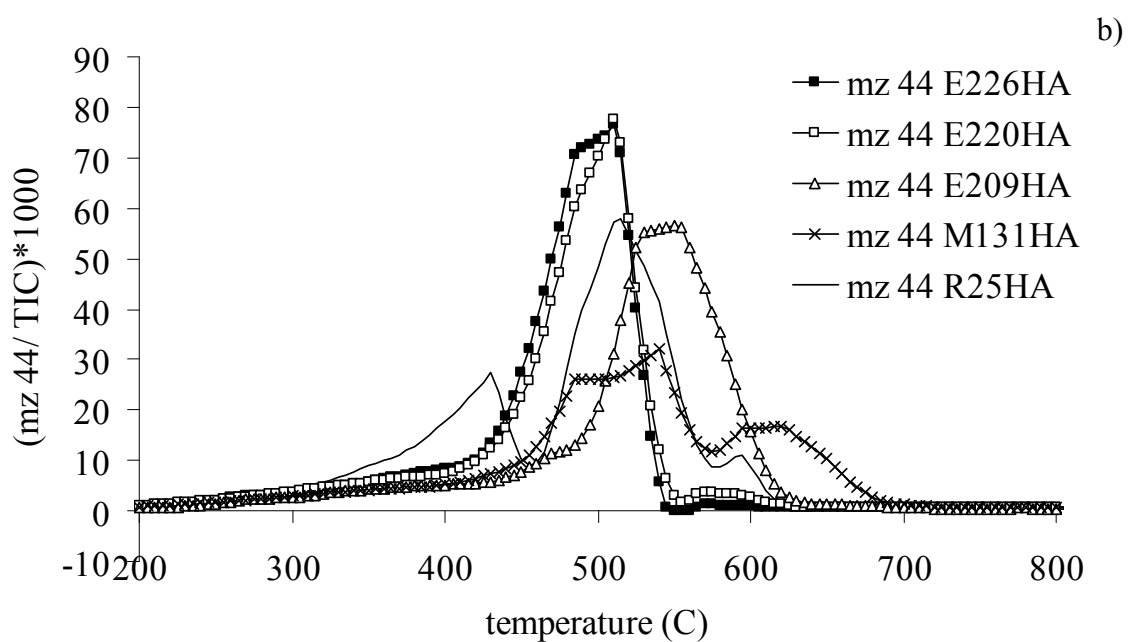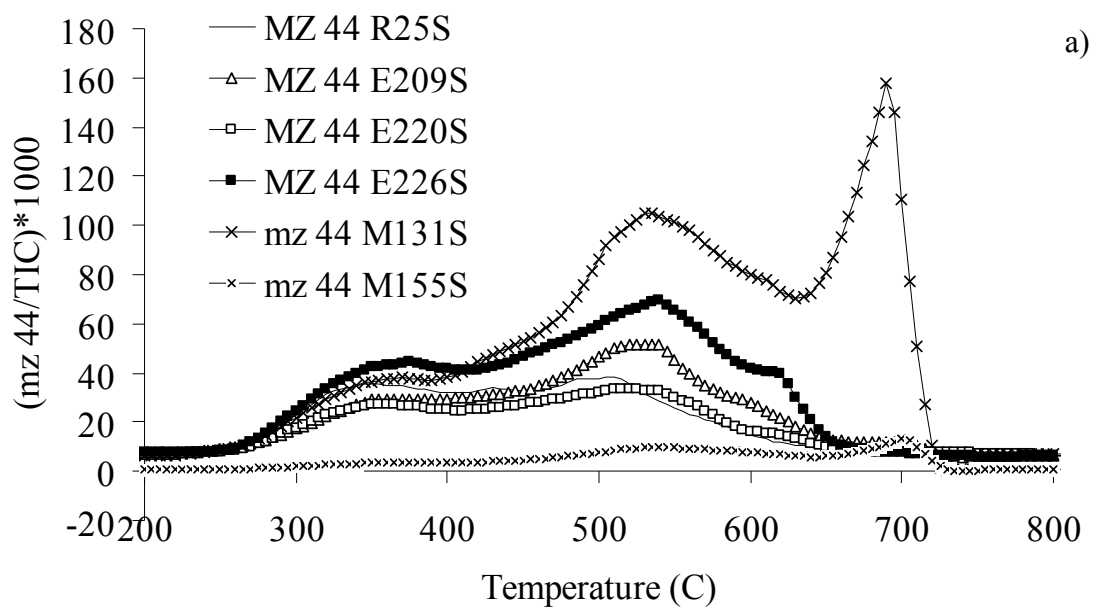
Figure 3.Thermograms of ion current *m/z* 44 for (a) sediments and (b) humic acids, and *m/z* 18 for (c) sediments and (d) humic acids.
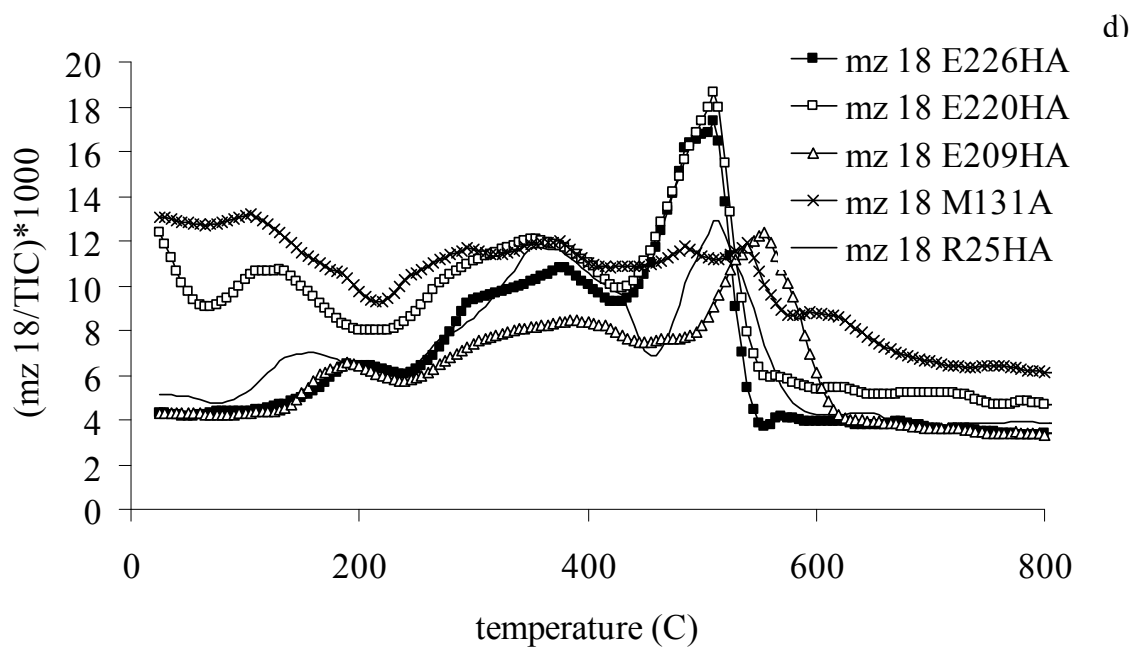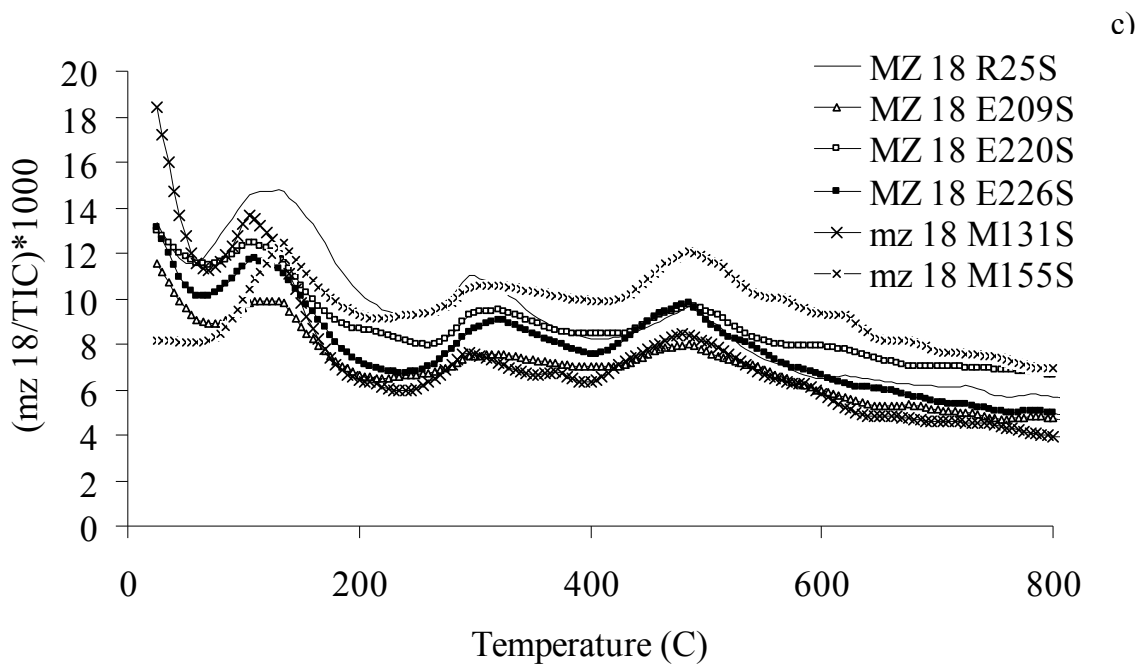
c)

d)

Figure 4 $\delta^{13}C_{\text{v-PDB}}$ values of sediments at various temperatures during thermal degradation (determined by TG-DSC-IRMS)
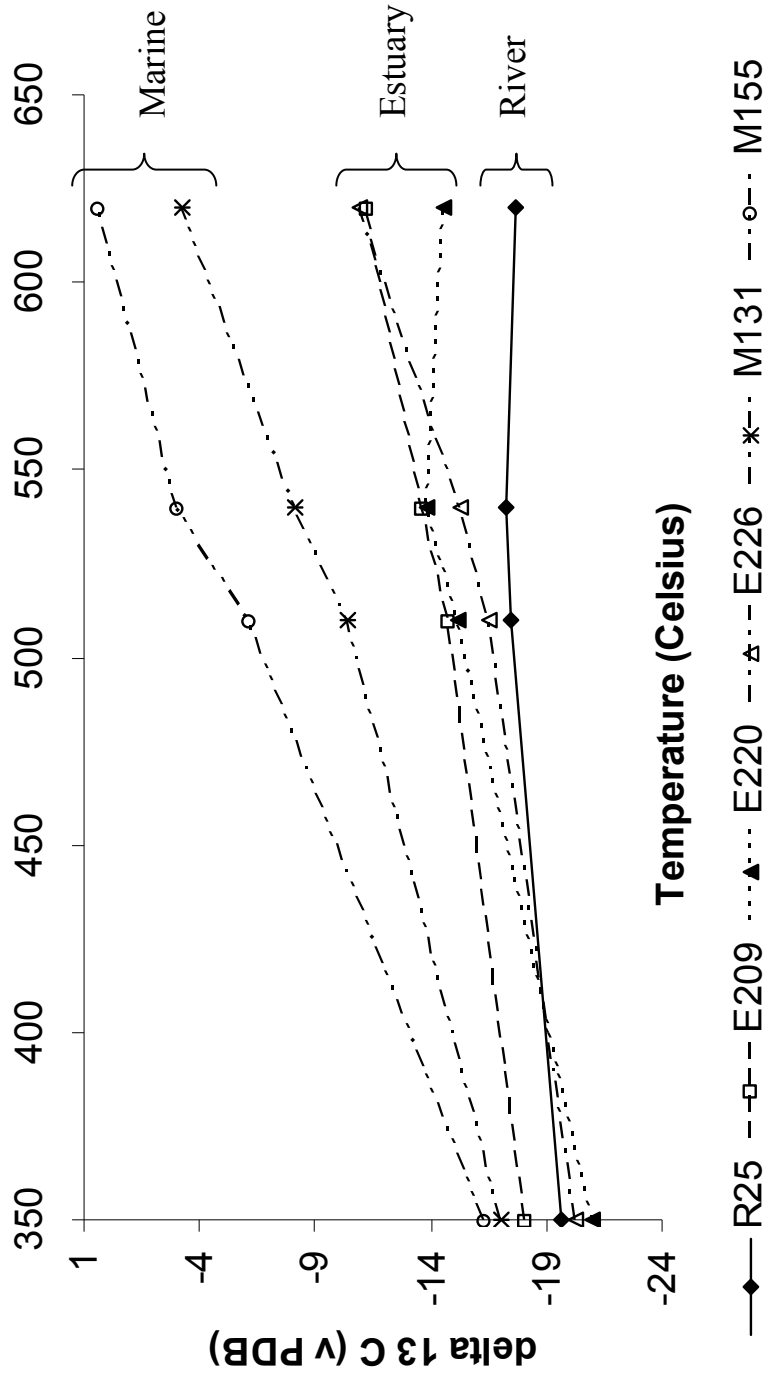
Figure 5 $\delta^{13}C_{v\text{-PDB}}$ values of humic acid fractions at various temperatures during thermal degradation (determined by TG-DSC-IRMS)