Available online at www.sciencedirect.com
ScienceDirect
Thermochimica Acta 458 (2007) 11–17
thermochimica acta
www.elsevier.com/locate/tca

Calorimetry and soil

N. Barros *, J. Salgado, S. Feijóo

Department of Applied Physics, Faculty of Physics, University of Santiago de Compostela, 15782 Santiago de Compostela, Spain

Available online 17 January 2007

Abstract

This paper is a review about the application of calorimetry to study soil properties and its metabolism. Although this research has increased slowly but continuously during the last 30 years, it is true that it has received poor attention. One reason for that could be the complexity of the soil and the difficulties to investigate it from a thermodynamic point of view. In this paper we would like to demonstrate that calorimetry constitutes a very suitable method to face the main topics related to soil quality and activity. Very well known indicators used in soil research can be measured by different thermal and calorimetric methods such as differential scanning calorimetry (DSC), thermogravimetry (TG) and isothermal calorimetry (ITC). TG and DSC are both temperature scanning methods used for estimation of certain properties of the soil material such as organic matter, ignition temperature, humification index, quartz content, so on, whereas the study of the soil microbial metabolism is conducted under essentially isothermal conditions by ITC. In this review, the contributions of these techniques to different topics in soil research are described and their importance for the environmental concern is discussed in the light of this new era.

Keywords: Differential scanning calorimetry (DSC); Thermogravimetry (TG); Isothermal calorimetry; Soil

> "The most basic relationship in microbial ecology is undoubtedly that between the quantity of matter and energy available to a microorganism from its environment and the quantity of growth that can be obtained from it." (E.H. Battley, 1987).

1. Introduction

Soil, calorimetry and thermodynamics have always been a very controversial conjunction for two reasons. First, soil constitutes a very complex system that it is difficult to face from a thermodynamic point of view. Second, the role of calorimetry in soil research is not well established yet. Many different topics are associated with soil analysis and, before applying calorimetry to these studies, it is necessary to find the aspects of that investigation for which calorimetry can be advantageous. Therefore, it is necessary to understand what constitutes an indicator of soil quality and of soil state. This is of extreme importance due to the significant decline in soil quality occurring worldwide by adverse changes in its physical, chemical and biological properties, and by the contamination caused by inorganic and organic chemicals [1]. At the International Conference on the Assessment and Monitoring of Soil Quality held at the Rodale Institute [2], Parr [3] proposed a quality index (SQ) that included the soil properties, the potential productivity, the environmental factors, the health, the erodibility, the biological diversity, the food quality/safety and the management inputs. It is clear that no method can provide such a wide range of factors. This is one of the reasons why this research constitutes by itself a huge area of study that is very difficult to deal with as a whole.

Soil quality indicators refer also to measurable attributes that reflect the capacity of soil to obtain crops or its sensitivity to environmental changes. The measurable attributes that are primarily influenced are soil depth, organic matter, respiration, aggregation texture, bulk density, infiltrating-nutrient availability and retention capacity. Changes in soil quality can be assessed by measuring appropriate indicators and comparing them with some reference values to provide information on the effectiveness of the selected farming system, land use practices, technologies and policies. Any practice that results in a negative contribution to any of the selected indicators could be considered unsustainable [1].

Can calorimetry deal with all these problems? We think so. First, calorimetry permits us to monitor the soil microbial activity continuously during long periods of time without disrupting the system, giving qualitative and quantitative indicators that inform us about the soil state and the soil disruption. Second,

* Corresponding author. Tel.: +34 981 563100x1404.
E-mail address: fanieves@lugo.usc.es (N. Barros).

0040-6031/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2007.01.010

it constitutes a very suitable method to obtain five of the eight indexes mentioned above. This is an enormous advantage since few methods can embrace such a wide range. Besides, it has already been successfully applied to study different aspects of soil such as: (i) changes in the organic matter that define soil fertility and structure, (ii) pesticide and water retention, (iii) the respiration by monitoring the biological activity, (iv) process modelling, (v) biomass activity estimations and (vi) early warning of the management effect on organic matter.

This paper is a review about the application of the calorimetric and thermal methods to the above mentioned topics during the last 30 years. It is explained how differential scanning calorimetry (DSC) and thermogravimetry (TG) have been mainly used to evaluate the changes that occur in soil organic matter (SOM), while isothermal calorimetry (ITC) has been applied to the study of soil microbial metabolism. It is also described the development of these methodologies to provide thermal and calorimetric indicators of soil quality and activity by the analysis of DSC, thermogravimetric and power–time curves and their main contributions to soil research.

2. Changes in soil organic matter

2.1. Contributions of calorimetry

The organic matter in soils consists of a mixture of plant and animal residues in various stages of decomposition, of chemical and biologically synthesized substances from the breakdown products, and of microorganisms, small animals and their decomposing remains. SOM could be considered the largest pool of terrestrial organic carbon (C), acting as a sink or a source of C.

The use of thermal techniques to study SOM started in the 1960s. Schnitzer, Hoffman, Skinner and Tan [4–7] used TG as a complement to other techniques to analyse organo-metallic complexes of soils and to obtain the first quantification of SOM with the purpose of classification.

In the 1970s, DTA and TG started to be used in the analyses of SOM and its chemical composition. DTA measures the difference in temperature between the soil sample and a reference when both are heated in a defined atmosphere at constant pressure [8,9]. The temperature difference is plotted against the programmed temperature or against time, but it is not possible to make a simple conversion of peak areas into energy units, which is the main problem of this technique. Even so, it has been widely used to obtain information about the thermal behaviour of SOM [10–17], although, due to its complexity, the interpretation of the curves and the relation with the process that takes place are not yet completely clear.

In the 1980s DTA was improved by fitting the apparatus with individual heaters for sample and reference, which made it possible to record the difference in heat exchange between the sample and the reference, while both remain at the same temperature during the heating at a predefined rate (the power compensation principle). DSC measures energy, not temperature differences [8,9], which is a very important feature. The results obtained using DTA and DSC were similar in all the cases, but

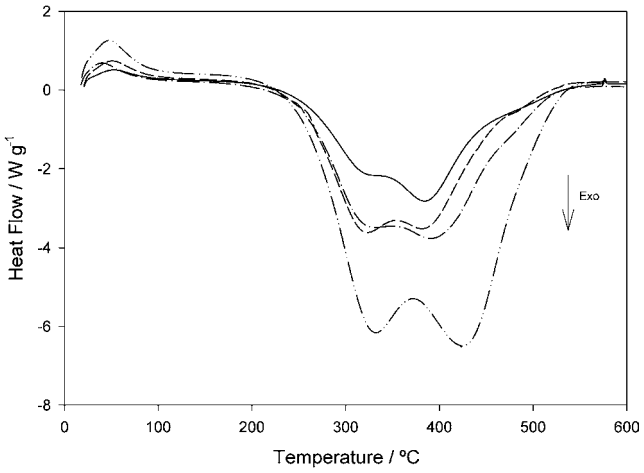

Fig. 1. Overlapping of DSC curve of four Galician (NW Spain) soil samples.

DSC provides important additional information, since it can give quantitative information about SOM. For instance, Fig. 1 shows the DSC curves of four Galician (NW of Spain) soil samples under atmospheric air, heating scanning rate of 10 °C/min. All soil are Humic Cambisol, very typical soil from this region. Sampling collection (0–5 cm deep) was done after removal of the litter layers, before de analysis, visible plant particles were removed by hand and sampled were sieved at 2 mm. The fraction less than 2 mm was homogenised and used for the study. Three well defined peaks can be observed in this curve: the first one, endothermic, from room temperature to 100 °C, is attributed to dehydration and to the loss of the most volatile substances; the second peak, exothermic from 200 to 570 °C, is due to the combustion of organic matter; and the third peak, endothermic at 575 °C, is due to the polymorphic transformation of quartz from the hypothermic to the hyperthermic state [18,19] (this peak is practically invisible in soils with high organic matter content).

The most interesting peak in the soil survey is the exothermic peak [11–17,19–27] which is due to the overlapping of two exothermic processes at diverse temperatures. Different authors have used various names to refer to these processes. For example, Dell'Abate et al. [22,25] and López-Capel et al. [27] named these peaks EXO_1 and EXO_2, while Satho [11,12] called them LER and HER, as abbreviations for the lower and the higher exothermic reaction, respectively. The first one, EXO_1 or LER, gave a minimum at approximately 300 °C due to the decomposition of more labile aliphatic and carboxylic groups, whereas the second one, EXO_2 or HER, which gave a minimum at approximately 400–450 °C, is due to the loss of more aromatic Bracewell and Robertson [10] found that the resolution in these exothermic peaks decreased when the degree of humification increased. Keeping the heterogeneous nature of the organic matter in mind and its stepwise, rather than continuous combustion, the positions of the peaks could shift slightly towards higher temperatures with increasing scanning rate [28].

Salgado et al. [19] determined the combustion enthalpy of SOM by DSC curves under flowing dry air, with a heating rate of 10 K min^{-1} and from room temperature to 600 °C. The integration of the peak areas in these curves gave the heat absorbed or

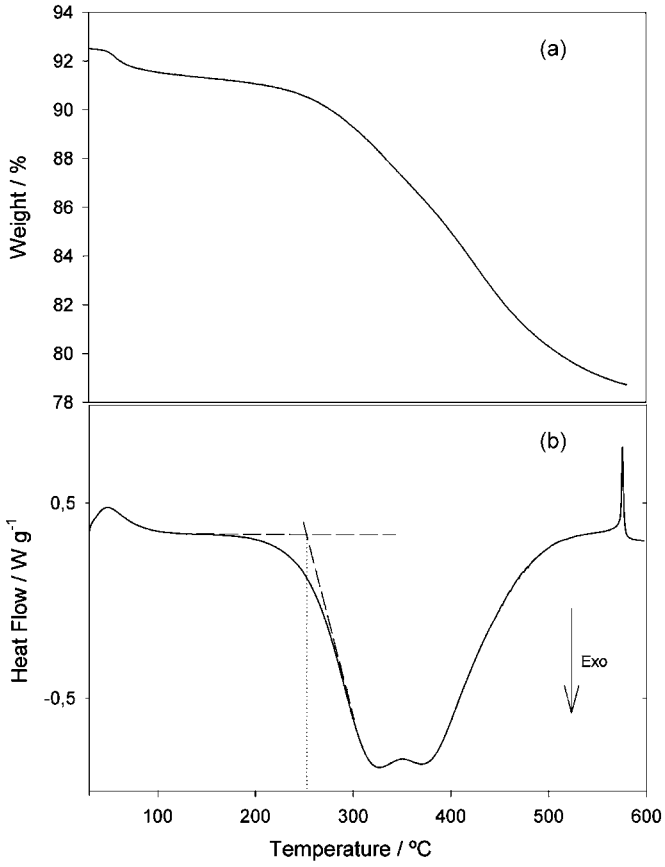

Fig. 2. Comparison between the simultaneously obtained TG (a) and DSC (b) curves of a soil sample and representation of the intersection point that gives the ignition temperature.

released in the corresponding process. In this way, the enthalpy of combustion of SOM was calculated by integration of the exothermic peak area.

TG is also a very useful technique for soil research [4–7,14,15,17,19,22–30]. It measures the weight loss of a sample soil during the combustion process, which temperatures of beginning and ending are perfectly defined by DSC of this soil, and it was found that it is directly related to the organic matter content [19].

2.2. Applications of the DSC and TG

2.2.1. Determination of the ignition temperature

The ignition temperature is defined as that value from which the combustion of organic matter proceeds continuously. When soil reaches this temperature, there is an irreversible loss of organic matter. The ignition temperature coincides with the beginning of the combustion peak and can be estimated from the DSC curves of the soil as the temperature of intersection between the baseline and the tangent to the inflexion point on the left side of the combustion peak (Fig. 2b). This parameter was calculated in several soils of Galicia (NW Spain) and values were between 230 and 240 °C [21]. The ignition temperature should be seriously considered as an important property for soils threatened by wildfires.

2.2.2. Determination of the quartz content

The last endothermic peak [19,21,29] in the soil DSC curves, at 575 °C, is due to the phase transition in quartz (α to β). The content of quartz (C_{quartz}) can be calculated using the following equation:

$$C_{quartz} = \frac{\Delta h}{\Delta h_0} \quad (1)$$

where Δh is the enthalpy, in J/g, associated with this process and measured by integration of the DSC curve, and Δh_0 is the standard enthalpy change of pure quartz mineral, which is 7.5 J/g [29].

The existence of this third peak permits a deeper analysis of the soil thermogram obtained under certain conditions, and it could also give important information for the characterization of archaeological materials found in soils [31].

2.2.3. Determination of the organic matter content

The organic matter content can be calculated using a thermogravimetric analyser. As was mentioned above, this apparatus measures weight changes in a soil sample as a function of temperature or time; the soil organic matter content can be calculated easily and quickly from the weight loss.

Fig. 2a shows the thermogravimetric curve of a soil sample with its weight loss due to heating as function of scanning temperature; the higher loss occurs approximately between 200 and 600 °C. This agrees with the temperature range for the combustion of organic matter, previously determined by DSC (Fig. 2b). This temperature interval coincides with results from other research in coals [30], soils, organic fractions from composite samples and forest combustibles [32]. Therefore, the organic matter content can be obtained as the difference between the weight loss determined in the above conditions and the initial soil weight.

2.2.4. Humification index

The overlapping exothermic peaks of the DSC curve can be used to estimate the relative abundance of more or less labile C. It is calculated as the ratio between the enthalpy of combustion of LER and HER, or as the ratio of weight loss obtained by TG between these two peaks.

2.2.5. Determination of the loss of organic matter due to wildfires

DSC and TG can inform us about the loss of organic matter after wildfires. It can be calculated as the difference between the combustion enthalpies of the organic matter in unburnt and burnt soil, or as the difference between the organic matter content of the unburnt and burnt soil [19].

3. Soil microbial metabolism

3.1. Calorimetric contributions

ITC calorimetry has been widely applied to the study of soil metabolism. Its beginning in 1973 [33] was closely linked to the development of new calorimeters adapted to study “the

life processes" [34,35], especially those of the heat conduction type. This early application can be attributed to Mortensen et al. [33] who defined in that paper two of the main topics: "the nutrient supply to soil results in an immediate increase in heat production that may possibly reflect an increase in the active microflora"; and "it is not always possible to measure all samples at once for practical reasons. It is therefore of great interest to determine how storage affects the microbial activity". The first one constituted the springboard to the development of ITC calorimetry for the study of soil microbial reactions, after solving some technological problems associated with the design of the calorimeters [36,37]. The second one has been poorly investigated. There was an attempt in as late as 1994, but with little conclusive results [38]. Even now, in 2006, it still constitutes a topic that would deserve serious consideration because of the lack of thermodynamic information.

The development of calorimetry applied to soil during the 1980s was strongly influenced by the calorimetric studies in microbiology and by two of the big soil research topics of that time. The first one was the understanding of the glucose degradation kinetics in soil [39], which was a consequence of previous studies suggesting the existence of a connection between the soil biomass activated with glucose and respiration [40,41]. The second one was the development of new methods to measure soil biomass and activity. During the late 1970s and the 1980s, many techniques were introduced, such as respirometry, determinations of ATP and enzymatic activities. ITC was one of them and provided important information in both topics. Its contribution to the understanding of the glucose degradation kinetics in soil started from 1983 to 1985, and was carried out by the Japanese group of Takahashi and co-workers. They explained the influence of the temperature on the soil glucose degradation reaction and published an "apparent Gibbs energy change", ΔG, that ranged from 76.7 ± 0.5 to $76.9 \pm 0.5\,\mathrm{kJ\,mol^{-1}}$, for temperatures from 298.15 to 308.15 K [42]. Later, in 1997 the group of Nuñez [43] in Spain used that model to determine a range of ΔG values from 98 to $102\,\mathrm{kJ\,mol^{-1}}$ for the same temperature range and the same reaction in a soil from Galicia. Until now that is the only information available about the Gibbs energy changes associated with the soil metabolic reactions.

The Japanese group [44] also demonstrated that the heat evolution observed during incubation of soil with glucose was associated with the increase in the amount of viable biomass that grew by consuming glucose as the energy source. They also showed the first quantitative analysis of the power–time curves to provide quantitative indicators of the soil microbial activity associated with carbon mineralization. They gave values for "the average heat evolution for the formation of an unit cell", symbolized as ω, "the average heat evolution per unit of glucose degraded", α, and "the apparent microbial growth rate constant", μ [44]. Those indices fitted well with those reported for different microorganisms by Lamprecht [45] and by Dermoun and Belaich [46]. We agree with the conclusion of the Japanese group in their studies "We believe that the method presented here might be one of the potential tools to predict quantitatively the biological activity of ecological systems".

Almost at the same time, Sparling [47] provided important information about the connection between the calorimetric measurements and the different methods employed in research on the soil activity and the biomass at that time. He measured the heat flow rates of different soils and compared them to the biomass data obtained by fumigation and respiration, to the basal respiration measured as the CO_2 accumulated in a sealed glass vessel containing the soil sample, and to the ATP content of the soils using trichloroacetic acid–paraquat–phosphate extractant [47]. He concluded that "... the good correlation of the microcalorimetric values with respiration and to a lesser extent with ATP content, amylase activity and biomass, indicates that microcalorimetry is a useful additional technique to estimate the catabolic activity of the soil populations". He also gave the relationship between the heat output and the soil biomass [48] and provided an equation and an experimental procedure to quantify the active soil biomass by calorimetry: 1 g biomass $C = 180.05 \pm 34.61$ mW [49]. All these papers settled a very solid basis for the development of calorimetry in soil research.

In 1994, the Nuñez group [50] applied the developments of Takahashi et al. [42,44] to study the kinetics of glucose uptake in Galician soils and found the data fitted well with the earlier findings. In 1994 too, Airoldi's group in Brazil reported a comparative study of the glucose uptake in four Brazilian soils and provided a different model for the quantification of the microbial growth [51]. For that calculation they introduced an enthalpy change for the glucose degradation reaction of $-2762\,\mathrm{kJ\,mol^{-1}}$, assuming that all the glucose was oxidised to CO_2 and water. They did not consider the possible contribution of the newly formed biomass to the enthalpy change, an aspect that was discussed by the Japanese and the Spanish groups, who reported enthalpy changes (called at that time "the average heat evolution per unit of glucose degraded") of 1287 [44] and $1447\,\mathrm{kJ\,mol^{-1}}$ [50], respectively. That is almost half of the enthalpy change assumed by [51]. The model developed by Takahashi et al. [44] has the advantage of being based on the experimental demonstration of the connection between the heat evolution rate and the microbial growth in soil. The latter constitutes also a very well known relation in microbiological calorimetry. These relations and their involvement in the kinetics of soil glucose uptake were again revised by Nuñez's group in 1999 [52].

The fact that the microbial growth rate constant and the heat evolution rate could be used as indicators of soil microbial metabolism stimulated the development of some work focused on the sensitivity of those indexes to the different soil treatments and properties, such as storage conditions [38], humidity of the soil samples [53], and different intrinsic soil properties in comparative studies [54,55].

At the same time there was an increasing interest in the study of the thermodynamics of soil microbial reactions. The main goal was to determine the enthalpy change of the reaction stimulated by glucose addition. The previous results obtained by the Japanese and Spanish groups, together with the great step forward of the development in the thermodynamics of microbial growth [56,57], gave strong evidence that microbial growth and the glucose oxidation reactions can be coupled, which means that the enthalpy change of that reaction could give quantitative

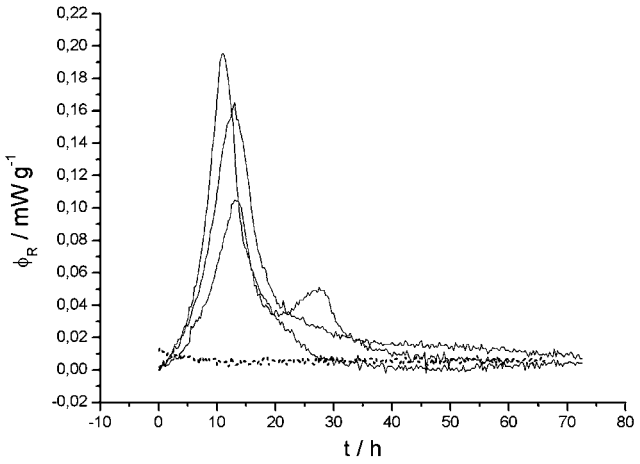

Fig. 3. Typical exothermic power–time curves showing microbial growth reactions recorded from 1 g of three different soil samples amended with 0.2 ml of a nutrient solution containing 1.5 mg glucose and 1.5 mg ammonium sulphate. One gram of soil sample amended with 0.2 ml of distilled water is used as reference. The integral of this curve yields the total heat evolution Q_T of the microbial growth reaction. These curves show differences due to the different nature of the samples and can be quantitatively analysed nowadays. The thickest doted line was obtained from one unamended sample and represents the soil basal metabolism. This plot has a very different shape if compared to those obtained after glucose amendment (unpublished data).

information on the carbon turnover in soil. This is a very desirable information in soil research even now, which otherwise could be only obtained by the introduction of labelled substrates in soil and by the use of very laborious methods [58,59]. It was possible for ITC to provide the same information in a fast, easy and ecological way. At that moment it was not easy to perform the calculation in soils due to the complexity of the microbial growth medium. It was necessary to isolate the microbial growth reaction first and then to find the appropriate model. The first attempts were shown in several papers from 1997 to 2001 [55,60–62] in which was given an interpretation of the enthalpy change of the glucose degradation reaction. Some models were proposed in these publications to calculate the enthalpy change based on the assumption that all the glucose added to the soil was completely oxidised to CO_2 and water, and that the anabolic reactions contributed little to that balance, according to the widely accepted thinking by Forrest [63]. Thus it was made possible to quantify that enthalpy change by the following equation [62]:

$$\Delta_r H_S = \frac{Q_T}{S_0} \quad (2)$$

where Q_T represents the total heat evolution in J/g soil. As shown in Fig. 3, it is calculated by the integration of the area limited by the power–time curve recorded after the glucose amendment. S_0 represents the quantity of glucose added to the sample.

The studies of Battley [56] and von Stockar et al. [57] during the 1980s and 1990s showed that Forrest did not consider in his investigations the influence of the degree of reduction of the carbon source on the microbial growth thermodynamics. This feature made it necessary to introduce the increment of biomass as a product of the glucose degradation reaction in microbial systems [57], since it contributes to the overall energy and mass balance and affects the enthalpy change of that reaction. That was clearly demonstrated in studies performed with different microorganisms using bioreactor calorimeters [57]. Therefore, it was necessary to revise the previous models given for soils in Eq. (2).

In 2003, Barros and Feijóo [64] showed a new thermodynamic model based on calorimetric measurements that informs quantitatively about the carbon turnover in soil. They reported an experimental calorimetric procedure to isolate the soil microbial reaction stimulated by the addition of glucose. The chemical reaction to be considered for the mass and energy balance is as follows:

$$aC_6H_{12}O_6 + bNH_4^+ + cO_2 = CH_{1.8}O_{0.5}N_{0.2} + dCO_2 + eH_2O + fH^+ \quad (3)$$

where $CH_{1.8}O_{0.5}N_{0.2}$ is the reported formulae for the microbial biomass. This balance is based on the proportionality between the heat evolution rate and the increment in biomass that permits the calculation of the heat yield of that reaction. Some important previous experiments for the development of this balance in soil were the determination of the combustion enthalpy of different microorganisms [65], and the direct correlation, experimentally demonstrated, that exists between the CO_2 release, the oxygen uptake and the heat dissipation of the soil microbial reactions [47,66–69] which satisfy the elemental basis for the mass balance. The energy and biomass yields computed by this method appear to be sensitive to changes in land use and could be considered as bioindicators of microbial quality and as an early warning of soil deterioration.

3.2. Calorimetric applications

3.2.1. Soil microbial metabolism and pollutants

A calorimetric method was developed for soil research at the same time as some applications appeared for studies on how the soil microbial metabolism was affected by land use and especially by the addition of different pollutants. Most experiments used the microbial growth rate constant, μ, and the total heat evolution of the microbial reaction, Q_T, as indicators to assess the effect of animal wastewaters [70], heavy metals and pesticides [66,71,72]. Most of these publications showed the effect of such pollutants on the microbial kinetics of glucose uptake as a reduced heat production and as a decrease in the microbial growth rate. These results were in many cases accompanied by CO_2 data that usually followed the same trend as that observed for the heat.

3.2.2. Soil bioremediation

Calorimetry appears to be useful for studying the bioremediation of polluted soils [73,74] by the calculation of the latency time, τ, together with the total heat and the kinetics of microbial growth. Bioremediation constitutes also a huge area of research and the calorimetric results do not show a general trend. The most important finding of these investigations was that the calorimetric indices showed differences among vari-

ous soil treatments, and therefore can be used to assess the bioremediation process.

3.2.3. Comparative studies

Some authors showed the usefulness of the soil microbial growth rate and total heat indices in comparative studies involving several soil samples, both for the assessment of the soil state and for the effect of deforestation and forestry reforestation [75,76]. In these works it was shown that calorimetry can give an alert about the negative impact on the soil microbial quality of certain forest species.

On the whole, the total heat evolution and the microbial growth rate seem to be the most widely employed calorimetric indices in soil research. They fit well with parallel CO_2 measurements and are sensitive enough to soil perturbation. They also have the advantage of being easily determined by calorimetry, providing an easy interpretation of the results.

4. Future trends

As can be seen, calorimetry has been involved in many of the main topics of soil research, giving its own data and contributing to the overall picture in combination with the other methods involved in this subject. Great questions about soil still exist and new topics constituting interesting challenges for calorimetry have been introduced in the beginning of the 21st century. This century is strongly influenced by the environmental policy related to the accumulation of CO_2 in the atmosphere and the sequestration of carbon. The Kyoto Protocol defined soil as responsible for 20% of the CO_2 released to the atmosphere, advocating for the control of land use to diminish the global warming. That control means to introduce new methods providing the necessary information in a rational and ecological way. Calorimetry may again play its role in this topic through the study of the soil microbial reactions from a thermodynamic point of view. An interesting option would be the development of mass and energy balances adapted to the soil glucose degradation reaction coupled to microbial growth [64]. This would be a very easy way to inform about the carbon kinetics. The potential of energy balances recently has been shown for assessing the effect of new chemical fertilizers on CO_2 release and on the capacity to retain carbon in soils, as is requested by the Kyoto Protocol nowadays [77].

Another point to be considered is that the soil research accepts the usefulness of glucose to study the capacity to mineralize external carbon sources. But its connection to SOM degradation is not yet well understood. Some information about the SOM biodegradability and its connection to carbon and nitrogen mineralization and to the microbial community has started to appear in the literature [78,79]. There is also some effort to study the SOM degradation by calorimetry using new indices calculated from unamended samples that seem to be sensitive to the main biological and physico-chemical properties of soil [80]. Some thermodynamic models that have been reviewed recently based on Thornton's rule could also be useful for the SOM degradation investigation [81]. Its connection with the soil carbon mineralization studied by the addition of glucose is still an unexplored field. We believe that both ITC and DSC have much to contribute to this new challenge. The connection between the organic matter and the soil respiration could be easily explored by the calculation of the combustion enthalpy of the organic matter as shown by DSC, and could be compared to the soil biomass data and activity indices also evaluated by ITC. In this sense, recent evidence shows that it is possible to stimulate a microbial growth reaction by the addition of complex organic sources to the soil. This stimulation is detected by calorimetry as an increase in the heat flow rate that correlates with the increase in biomass measured by fumigation and by the most probable number method, and with the CO_2 evolution [82,83]. The use of DSC to evaluate the combustion enthalpy of these organic carbon sources would permit the development of mass and energy balances that provide information about the effect on carbon turnover, and therefore on global warming. We also would like to mention here that the thermodynamics of the soil reactions are not well known. It would be really interesting to search for models that provide the Gibbs energy in comparative studies, especially to obtain the entropy of these reactions and to contribute to the understanding of the entropic changes associated with the microbial growth.

Acknowledgments

The authors are especially thankful to Ingolf Lamprecht and Richard Kemp for supporting and assessing this review. We also thank to Lee Hansen for his kindly invitation to make this paper and to J. R García Menéndez and his group for close collaboration and finance support.

References

[1] M.A. Arshad, S. Martin, Agriculture, ecosystems and environment 88 (2002) 153–160.
[2] Rodale Institute, in: Proceedings of the International Conference on the Assessment, Monitoring Soil, Quality, Conference Report, Abstracts, Rodale Press, Emmans, PA, USA, 1991.
[3] J.F. Parr, R.I. Papendick, S.B. Hornick, R.E. Meyer, Am. J. Alternative Agric. 7 (1992) 5–11.
[4] M. Schnitzer, S.I.M. Skinner, Soil Sci. 98 (1964) 197–203.
[5] M. Schnitzer, I. Hoffman, Geochim. Cosmochim. Acta 31 (1967) 7–15.
[6] M. Schnitzer, I. Hoffman, Soil Sci. Soc. Am. Proc. 30 (1966) 63–66.
[7] K.H. Tan, Soil Biol. Biochem. 10 (1978) 123–129.
[8] J.W. Dodd, K. Tongue, Thermal Methods, Wiley Interscience, London, 1987.
[9] G. Höhne, W. Hemminger, H.-J. Flammersheim, Differencial Scanning Calorimetry, Springer-Verlag, Berlin, 1996.
[10] J.M. Bracewell, G.W. Robertson, J. Therm. Anal. 8 (1975) 117–124.
[11] T. Satoh, Soil Sci. Plant Nutr. 30 (1) (1984) 1–12.
[12] T. Satoh, Soil Sci. Plant Nutr. 30 (1) (1984) 95–104.
[13] G. Giovannini, S. Lucchesi, M. Giachetti, Soil Sci. 149 (1990) 344–350.
[14] P. Leinweber, H.R. Schulten, C. Horte, Thermochim. Acta 194 (1992) 175–187.
[15] P. Leinweber, H.R. Schulten, Thermochim. Acta 200 (1992) 151–167.
[16] R.S. Rohella, N. Sahoo, S.C. Paul, S. Choudhury, V. Chakravortty, Thermochim. Acta 287 (1996) 131–138.
[17] H.A.A. Gibbs, L.W. O'Garro, A.M. Newton, Thermochim. Acta 363 (2000) 71–79.
[18] J.B. Dixon, S.B. Weed, Minerals in Soil Environments, 2nd ed., Published by Soil Science Society of America, Madison, Wisconin, USA, 1989.
[19] J. Salgado, M.M. Mato, A. Vázquez-Galiñanes, M.I. Paz Andrade, T. Carballas, Thermochim. Acta 410 (2004) 141–148.

[20] P. Buurman, J.D. Doesburg, M.L. Fernández Marcos, Marcos Humic Subs. Global Environ. Imp. Hum. Health, in: Proceedings of the 16th International Meeting Humic. Sust. Society, 1994, pp. 541–548.
[21] J. Salgado, M.I. González, J. Armada, J.M.I. Paz Andrade, M. Carballas, T. Carballas, Thermochim. Acta 259 (1995) 165–175.
[22] M.T. Dell'Abate, A. Benedetti, P. Sequi, J. Therm. Anal. Cal. 61 (2000) 389–396.
[23] M.R. Provenzano, A. Ouatmane, M. Hafidi, N. Senesi, J. Therm. Anal. Cal. 61 (2000) 607–614.
[24] M. Stenseng, A. Zolin, R. Cenni, F. Frandsen, A. Jensen, K. Dam-Johansen, J. Therm. Anal. Cal. 64 (2001) 1325–1334.
[25] M.T. Dell'Abate, A. Benedetti, A. Trinchera, C. Dazzi, Geoderma 107 (2002) 281–296.
[26] P. Melis, P. Castaldi, Thermochim. Acta 413 (2004) 209–214.
[27] E. López-Capel, S.P. Sohi, J.L. Gaunt, D.A.C. Manning, Soil Sci. Soc. Am. J. 69 (2005) 136–140.
[28] A.G.M. Vasandini, M.R. Shah, J. Therm. Anal. 41 (1994) 1053–1061.
[29] Q. Wang, M. Odlyha, N.S. Cohen, Thermochim. Acta 365 (2000) 189–195.
[30] X. Shu, X. Xu, H. Fan, S. Wang, D. Yan, Thermochim. Acta 381 (2002) 73–81.
[31] M. Odlyha, Thermochim. Acta 269/270 (1995) 705–727.
[32] S. Leodakis, d. Bakirtzis, A. Dimitrakopoulos, Thermochim. Acta 390 (2002) 83–91.
[33] U. Mortensen, B. Norén, I. Wadsö, Bull. Ecol. Res. Commun. 17 (1973) 189–197.
[34] I. Wadsö, Acta. Chem. Scand. 22 (1968) 927–937.
[35] I. Wadsö, Quart. Rev. Biophysics. 3 (1970) 383–427.
[36] K. Ljungholm, B. Norén, I. Wadsö, OIKOS. 33 (1979) 15–23.
[37] K. Ljungholm, B. Norén, I. Wadsö, OIKOS 33 (1979) 24–30.
[38] L. Nuñez Regueira, N. Barros, I. Barja, J. Therm. Anal. Cal. 41 (1994) 1379–1383.
[39] P.N. Coody, L.E. Sommers, D.W. Nelson, Soil Biol. Biochem. 18 (1986) 283–289.
[40] G.P. Sparling, B.G. Ord, D. Vaugham, Soil Biol. Biochem. 13 (1981) 99–104.
[41] J.P.E. Anderson, K.H. Domsch, Soil Biol. Biochem. 10 (1978) 215–221.
[42] H. Yamano, K. Takahashi, Agric. Biol. Chem. 47 (1983) 1493–1499.
[43] L. Nuñez, I. Barja, Thermochim. Acta 303 (1997) 155–159.
[44] T. Kimura, K. Takahashi, J. Gen. Microbiol. 131 (1985) 3083–3089.
[45] I. Lamprecht, Growth and metabolism in yeasts, in: A.E. Beezer (Ed.), Biological Microcalorimetry, Academic Press, New York, 1980, pp. 43–112.
[46] Z. Dermoun, J.P. Belaich, J. Bacteriol. 143 (1980) 742–746.
[47] G.P. Sparling, Soil Biol. Biochem. 13 (1981) 93–98.
[48] G.P. Sparling, Soil Biol. Biochem. 13 (1981) 373–376.
[49] G.P. Sparling, J. Soil Sci. 34 (1983) 381–390.
[50] L. Nuñez, N. Barros, I. Barja, Thermochim. Acta 237 (1994) 73–81.
[51] S.A.M. Critter, J.A. Simoni, C. Airoldi, Thermochim. Acta 232 (1994) 145–154.
[52] I. Barja, L. Nuñez, Soil Biol. Biochem. 31 (1999) 441–447.
[53] N. Barros, I. Gómez-Orellana, S. Feijóo, R. Balsa, Thermochim. Acta 249 (1995) 161–168.
[54] N. Barros, S. Feijóo, R. Balsa, Thermochim. Acta 296 (1997) 53–58.
[55] N. Barros, S. Feijóo, J.A. Simoni, A.G.S. Prado, F.D. Barboza, C. Airoldi, Thermochim. Acta 328 (1999) 99–103.
[56] E.H. Battley, in: John Wiley & Sons (Ed.), Energetics of Microbial Growth, John Wiley & Sons, New York, 1987.
[57] U. von Stockar, L. Gustafsson, C. Larsson, I. Marison, P. Tissot, E. Gnaiger, Biochim. Biophys. Acta 1183 (1993) 221–240.
[58] M. Amato, J.N. Ladd, Soil Biol. Biochem. 24 (1992) 455–464.
[59] J.N. Ladd, J. Monroizer, M. Amato, Soil Biol. Biochem. 24 (1992) 359–371.
[60] N. Barros, S. Feijóo, S. Fernández, J.A. Simoni, C. Airoldi, Thermochim. Acta 356 (2000) 1–7.
[61] N. Barros, S. Feijóo, S. Fernández, J.A. Simoni, C. Airoldi, Entropie 224 (2000) 75–79.
[62] N. Barros, S. Feijóo, J.A. Simoni, S.A.M. Critter, C. Airoldi, J. Therm. Anal. Cal. 63 (2001) 577–588.
[63] W.W. Forrest, D.J. Walker, Adv. Microb. Physiol. 5 (1971) 213–274.
[64] N. Barros, S. Feijóo, Biophys. Chem. 104 (2003) 561–572.
[65] J.L. Cordier, B.M. Butsch, B. Birou, U. von Stockar, Appl. Microbiol. Biotechnol. 25 (1987) 305–312.
[66] A. Tancho, R. Merckx, R. Schoovaerts, K. Vlassak, Thermochim. Acta 251 (1995) 21–28.
[67] B.P. Albers, F. Beese, A. Hartmann, Biol. Fertil. Soils 19 (1995) 203–208.
[68] S.A.M. Critter, S.S. Freitas, C. Airoldi, Thermochim. Acta 410 (2004) 35–46.
[69] M. Raubuch, F. Beese, Soil Biol. Biochem. 31 (1999) 949–956.
[70] J.E. Dziejowski, Thermochim. Acta 251 (1995) 37–43.
[71] I. Lamprecht, C.H. Motzkus, B. Schaarschimidt, D. Coenen-Stass, Thermochim. Acta 172 (1990) 87–94.
[72] A.G.S. Prado, C. Airoldi, Thermochim. Acta 394 (2002) 155–162.
[73] L.E. Erickson, L.C. Davis, M. Narayanan, Thermochim. Acta 250 (1995) 353–358.
[74] P. Tissot, J. Therm. Anal. Cal. 57 (1999) 303–312.
[75] L. Nuñez, O. Nuñez-Fenández, J.A. Rodriguez Añón, J. Proupín, Castiñeiras, Thermochim. Acta 394 (2002) 123–131.
[76] L. Nuñez, J.A. Rodríguez Añón, J. Proupín Castiñeiras, Soil Biol. Biochem. 38 (2006) 115–124.
[77] N. Barros, C. Airoldi, J.A. Simoni, B. Ramajo, A. Espina, J.R. García, Thermochim. Acta 441 (2006) 89–95.
[78] B. Marschner, K. Kalbitz, Geoderma 113 (2003) 211–235.
[79] W.R. Cookson, D.A. Abaye, P. Marschner, D.V. Murphy, E.A. Stockdale, K.W. Goulding, Soil Biol. Biochem. 37 (2005) 1726–1737.
[80] N. Barros, S. Feijóo, S. Fernández, Thermochim. Acta 406 (2003) 161–170.
[81] L.D. Hansen, C. Macfarlane, N. McKinnon, B.N. Smith, R.S. Criddle, Thermochim. Acta 422 (2004) 55–61.
[82] S.A.M. Critter, S.S. Freitas, C. Airoldi, Thermochim. Acta 394 (2002) 133–144.
[83] S.A.M. Critter, S.S. Freitas, C. Airoldi, Thermochim. Acta 394 (2002) 145–154.